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ESTIMATION OF PARAMETERS FOR MODELING THE BEHAVIOR OF SELECTED PESTICIDES AND ORTHOPHOSPHATE

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A 3-year laboratory study was conducted to determine sorption and degradation of selected pesticides as well as sorption of orthophosphorus on several U.S. agricultural soils. The data obtained in the study permit the estimation of sorption and degradation parameters required in predicting nonpoint source loadings of pesticides and phosphorus from croplands. Nine pesticides (six herbicides and three insecticides) representing a broad range of chemical classes were studied. The pesticide studies were conducted with seven soil types; P-sorption was measured on 36 soils that are distributed widely across the United States.

Data suggest that sorption coefficient based on soil organic carbon is not only independent of soil type but also of soil particle size within a soil type. For all pesticides studied, microbial degradation rates followed first-order kinetics. Temperature and soil-water tension were the two soil environmental factors that showed a significant effect on pesticide degradation rates. Phosphate sorption constants in the Temkin equation were better correlated with several soil properties than were the coefficients in Langmuir or Freundlich equations. Ammonium oxalate extractable Al, ammonium acetate extractable Ca, and clay content were the three soil properties most useful in estimating Temkin equation parameters.

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FOREWORD

As envrironmental controls become more costly to implement and the penalties of judgment errors become more severe, environmental quality management requires more efficient management tools based on greater knowledge of the environmental phenomena to be managed. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Technology Development and Applications Branch develops management and engineering tools to help pollution control official achieve water quality goals through watershed management.

This report summarizes the results from a laboratory study to characterize sorption and degradation of selected pesticides in soils and sorption of orthophosphate on soils. The results presented in this report may be useful in estimating the parameters required in several process-oriented models for predicting nonpoint source pollution loadings from croplands.

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ABSTRACT

A three-year laboratory study was conducted to determine sorption and degradation of selected pesticides as well as sorption of orthophosphate on several U.S. agricultural soils. The data presented in this report permit estimation of sorption and degradation parameters required in predicting nonpoint source loadings of pesticides and phosphorus from croplands. Nine pesticides, six herbicides and three insecticides, representing a broad spectrum of chemical classes were studied. The pesticide studies were conducted with seven soil types while P-sorption was measured on thirty-six soils distributed widely across the U.S.

Data collected during this project suggest that pesticide sorption coefficient (K_{oc}) based on soil organic carbon is not only independent of soil type but also of soil particle-sizes within a soil type. Thus, each pesticide can be assigned a single K_{oc} value and given the organic carbon enrichment of the sediment, partitioning of pesticide between solution and sediment-phases during a given runoff may be estimated. For all pesticides studied, microbial degradation rates followed first-order kinetics. The rate coefficients (or half-lives) were not correlated with any of the following soil properties: soil organic carbon content, clay content, cation exchange capacity, pH, Eh, and total bacterial and fungal propagules. Temperature and soil-water tension (soil-water content) were the two soil environmental factors that did show a significant effect on pesticide degradation rates. However, for temperatures in the range of 15-35°C and soil water tensions in the range of 0.1-1 bar, degradation rate coefficients for a given pesticide were essentially constant. Considerable amounts of non-extractable "bound" residues were formed for all soil-pesticide combinations studied. Generally larger amounts of bound residues were found in moist soils (incubated at soil water tensions less than 1 bar) than in drier soils (at 15 bar tension).

Phosphate sorption was measured on 36 U.S. soils using a standardized protocol. Measured P sorption data were fitted to Freundlich, Langmuir, and Temkin equations. Phosphate sorption constants in the Temkin equation were better correlated with several soil properties than were the coefficients in Langmuir or Freundlich equations. Ammonium Oxalate extractable Al, ammonium acetate extractable Ca, and clay content were the three soil properties most useful in estimating Temkin equation parameters.

This report was submitted in fulfillment of Grant No. R-805529-03 by the University of Florida. This report covers the period November 1977 to July 81 and work was completed as of January 83.

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CHAPTER I

INTRODUCTION

The use of pesticides, especially herbicides, has increased significantly during the past three decades. These chemicals have contributed significantly to increase crop yields and in many cases have decreased production costs. However, the use of pesticides poses a potential threat to the environment and human health. Therefore, agricultural producers as well as environmental scientists are concerned with the fate of pesticides in agro-ecosystems. Consequently, information on pathways by which pesticides leave the site of application (i.e., croplands) and subsequently cause nonpoint source pollution will continue to be sought. Such data are essential to the development of appropriate controls and management technologies for minimizing nonpoint source loadings of pesticides from croplands.

A major pathway for pesticide removal from croplands, especially in terms of pesticide movement to nontarget areas, is in runoff water and on sediment carried along with the runoff water. The amount of soil-applied pesticide which leaves the field in this manner depends primarily on: 1) the intensity and the duration of rainfall event, and 2) the time lag between pesticide application and the runoff event. The depth of soil layer (i.e., mixing zone) from which pesticides are removed during a runoff event is determined by the intensity and duration of the rainfall event. The amount of pesticide available within this mixing zone is determined by the extent of pesticide dissipation that occurs between application and a given runoff event. Various processes governing the fate of pesticides in soils are: retention (adsorption-desorption), transformations (microbial and chemical degradation), and transport (overland flow, leaching, and volatilization).

Two approaches for estimating the edge-of-field nonpoint source loadings of pesticides are available. In the first, empirical relationships have been developed by correlating the quantities of pesticides available in the surface soil (0-1 cm) and the losses measured at the edge of the field. Such relationships have been reported recently by Leonard et al. (1979) and Wauchope and Leonard (1980). Obviously, such empirical relationships are developed based on extensive and often costly field measurements. Alternately, pesticide retention, transformation, and transport parameters can be used in several process-oriented nonpoint source simulation models that are presently available. Examples are the PTR and ARM models described by Crawford and Donigian (1974), Donigian et al. (1977) and the CREAMS model presented by Knisel (1979).

In this report, we will discuss results from a three-year laboratory study to measure sorption and degradation of selected pesticides and sorption of orthophosphate in U.S. soils. Seven soils from major agricultural areas in the U.S. along with nine pesticides were included in this study. These data were used to provide estimates of sorption coefficients and degradation rate coefficients for pesticides. Sorption of orthophosphate was measured on 36 U.S. soils. These data were used to determine soil factors influencing P-sorption on soils. The data presented in this report may be used to estimate parameter values required in various process-oriented simulation models for describing nonpoint source loadings of pesticides and orthophosphate from croplands.

CHAPTER II

CONCLUSIONS

PESTICIDE SORPTION:

Based upon the data collected during this project, the following justifiable simplifications for estimating pesticide sorption parameters are proposed:

1) Pesticide sorption on whole soils and soil size-separates is determined primarily by the soil organic carbon content. That is, the sorption partition coefficient based on soil organic carbon (K_{oc}) for a given pesticide is essentially independent not only of soil type but also of soil particle-size. Thus, the problem of predicting pesticide sorption by soils or the partitioning of pesticides between the sediment- and water-phases of runoff reduces to a more manageable problem of a single K_{oc} value for a pesticide and the organic carbon enrichment for a given runoff event. This approximation is more likely to be in error for ionic and ionizable pesticides such as 2,4,5-T.

2) The extent of sorption isotherm nonsingularity may be specified quantitatively using the index $\beta=(N_a/N_d)$, where N_a and N_d are the Freundlich isotherm constants, respectively, for the adsorption and desorption isotherm loops. Large β value indicates extensive nonsingularity, while $\beta=1$ suggests singular isotherms. Based upon β values, it was concluded that isotherm nonsingularity increased with increasing soil particle-size. For sand size-fraction (> 50 μm) β value was about 4, while for fine clay fraction $\beta=1$. Analysis of published sorption data for sediments supported this conclusion.

PESTICIDE DEGRADATION:

Two types of pesticide degradation rates were measured: mineralization rate based on $^{14}CO_2$ evolution and disappearance rate based on the loss of solvent-extractable parent chemical. Using these data, the following conclusions regarding pesticide degradation are suggested:

1) Pesticide degradation rates in soils could be described using the first-order kinetics. For each soil-pesticide combination, the degradation rate coefficient (k, day^{-1}) or half-life ($t_{½}$, days) could be specified.

2) For all pesticides studied, the disappearance rate was greater than the mineralization rate. The differences between these two rates are due to accumulation of intermediate metabolites, assimilation into microbial

biomass, and formation of "bound" residues. Of these, bound residue formation appears to be the major contributing factor.

3) Pesticide degradation rates were not correlated with soil organic carbon content, pH, cation exchange capacity, clay content, total bacterial propagules, and total fungal propagules. The two soil environmental factors that did influence pesticide degradation rates were soil-water content (or soil-water tension) and soil temperature.

4) Soil temperatures below 25°C had a greater influence on pesticide degradation rates than at temperatures above 25°C. Hence, activation energies (ΔE_a) for pesticide degradation between 15°-25°C were greater than those between 25°-35°C.

5) Pesticide degradation rates in soils maintained at 15 bar soil water tension were substantially lower than at 1 bar or lower. At tensions between 0.1 and 1 bar, degradation rates were not significantly different.

6) Soil water tension may influence oxygen tension and redox potentials in soils. As a result, the pesticide degradation pathway may be altered with changes in soil water tension, and different types of metabolites may accumulate.

7) Bound residues, i.e., nonextractable ^{14}C-residues, were found during degradation of all pesticides in all soils studied. The extent of bound residue formation, however, was different for each soil-pesticide combination. Generally, more bound residues were formed in moist soils (at 0.1, 0.33, and 1 bar tension) than in drier soils (at 15 bar tension).

PHOSPHATE SORPTION:

Phosphate sorption isotherms were measured on thirty-six soils which were distributed widely across the United States and represented seven soil orders. The sorption isotherms were measured using a standard protocol and certain modifications thereof including the use of 0.03 $\underline{M}$ KCl as the background electrolyte (to more closely simulate natural conditions) rather than 0.01 $\underline{M}$ $CaCl_2$ and no disinfectant. The proposed protocol is listed in Section V.3.4. We propose 0.03 $\underline{M}$ KCl as the background electrolyte when measuring phosphate sorption isotherms.

Regression analyses of the soil properties with the phosphate sorption parameters showed that constants in the Temkin equation were better correlated with soil properties than the Freundlich or Langmuir equations. The equations which were used to estimate the Temkin constants with the best correlation coefficients were functions of ammonium oxalate Al and clay content or ammonium acetate Ca and clay. Calculated confidence limits around each calculated isotherm, based on propogation of errors using the Temkin equation, indicated that ammonium acetate, extractable Ca content, and clay content could be used successfully to predict 72% of the sorption isotherms. Calculated isotherms were based solely on soil chemical and physical properties.

CHAPTER III

PESTICIDE SORPTION ON WHOLE SOILS AND SOIL PARTICLE-SIZE SEPARATES

P. S. C. Rao and P. Nkedi-Kizza

INTRODUCTION

The Freundlich equation, $S=KC^N$, has been used successfully for relating adsorbed-phase (S) and solution-phase (C) concentrations of pesticides at equilibrium; K and N are constants specific to a pesticide-soil combination. The extent to which a pesticide is adsorbed by a soil is determined by several physical-chemical properties of both the soil and the pesticide. Several researchers have shown during the past two decades that soil organic carbon (OC) content was the single best soil characteristic correlated with the K value for organic pesticides. In fact, for a given organic pesticide the sorption partition coefficient based on soil organic carbon, denoted by K_{oc} (equal to K/OC), was found to be fairly independent of soil type. This suggests that (i) soil organic carbon is the primary soil constituent responsible for pesticide sorption, and (ii) the role of soil organic carbon apparently varies only slightly among different soils. Rao and Davidson (1980) and Kenaga and Goring (1980) performed an extensive literature search and compiled the values for K, N, and K_{oc} for a large number of pesticides. Two implicit assumptions commonly made in using K_{oc} values for pesticides should be noted. First, the sorption isotherms are assumed to be linear; thus, any errors introduced by the nonlinearity in isotherms must be quantified. Second, because the adsorption and desorption isotherms are assumed to be singular, deviations from such ideal behavior (i.e., the effect of nonsingularity) must also be evaluated. Rao and Davidson (1980) noted that both types of errors are probably within a factor of 2 or 3 for most pesticides within the concentration range generally associated with agricultural applications ($\leq$ 10 mg/L). It is also important to recognize that the use of K_{oc} is convenient and expedient in an operational sense only and no inference as to the mechanisms of pesticide sorption on soils should be made.

During a runoff event, the finer soil particle-sizes are selectively carried off along with the runoff water resulting in an enrichment of the fines in the sediment delivered at the edge-of-field. Enrichment factors generally vary between 2 to 4 depending on the soil type and the size and intensity of the storm event (see for example, Leonard et al., 1979; Smith et al., 1978). The finer size fractions of the soil are usually characterized by higher organic carbon contents and larger specific surface areas (Leonard et al., 1979). From earlier discussion of pesticide sorption on whole soils, the finer size fractions might be expected to have a larger sorption partition coefficient (K) when compared with the coarser size fractions of the same soil. The important question here is whether different particle-size fractions of the same soil have a similar K_{oc} value for a given pesticide. This would imply that the role of the soil organic carbon is essentially the same among different particle-size fractions.

Karickhoff and Brown (1978) and Karickhoff et al. (1979) measured the adsorption of two pesticides (paraquat and methoxychlor) and several polycyclic aromatic hydrocarbons as a function of particle-size on several natural sediments. They found that adsorbed pesticide concentrations varied over several orders of magnitude among the individual particle-size fractions of a given sediment, with a pronounced preference towards the finer sizes. However, for the uncharged compounds the differences in amounts adsorbed were directly proportional to the organic carbon content of a given particle size. Based on these findings they proposed that the K_{oc} value, i.e., the adsorption coefficient normalized with respect to organic carbon content, for all particle-size separates was essentially the same for a given nonionic pesticide. In this study, their work is extended to several other pesticides using soils from several geographical locations in the U.S.

MATERIALS AND METHODS

Seven soils, representing the major U.S. agricultural areas, used in this study were: Cecil loamy sand (Typic Hapludults), Grenada silt loam (Glassic Fragiudalfs), Houston clay loam (Typic Chromuderts), Eustis fine sand (Typic Quartzipsamments), Sharpsburg silt clay loam (Typic Aqiudolls), Webster silt clay loam (Typic Haplaquolls), and Yolo silt loam (Typic Xerorthents). Selected properties of these soils as well as the state from which they were collected are listed in Table III-1. These seven soils were chosen for this project not only because of their agricultural significance but also because of the broad representation in organic carbon contents and type and content of clay minerals. Furthermore, some of these soils may serve as "benchmark" soils because considerable data on pesticide and water behavior in these soils (e.g., Webster, Eustis, Cecil) have been collected in an earlier study (Davidson et al., 1980).

The soils were separated into two size fractions: sand (50-2000 μm) and fines (<50 μm). The particle-size separation procedures were similar to those of Jackson (1974) except that no oxidizing agents were used to destroy the soil organic carbon. The soil was dispersed in sodium bicarbonate solutions and the sand fraction was recovered by sedimentation and the clay plus silt size-fractions, referred to here as the "fines", remaining in the supernatant solution were recovered by centrifugation after flocculating with $CaCl_2$. Both the sand and fines were washed with sufficient $CaCl_2$ solutions until Na^+-free. For a detailed investigation of the particle-size effect on pesticide sorption, the Webster soil was separated into: sand, medium silt, coarse silt, and coarse clay fractions.

Organic carbon content (%OC) of the whole soils and the soil size-separates was determined by a dry combustion method using a Leco Analyzer; Soils suspected to contain free $CaCO_3$ were acid-treated prior to combustion analysis. OC contents of the whole soils and size-separates from each soil are listed in Table III-1.

Nine pesticides included in this study were: atrazine, cyanazine, metribuzin, diuron, propachlor, 2,4,5-T, carbaryl, carbofuran and fonofos. As shown in Table III-2, this list represents pesticides with a broad range in chemical structures, aqueous solubilities, and crystal energies (melting points). These compounds are used extensively for pest management in corn and cotton grown in the regions where the seven project soils shown in Table III-1 were collected.

Pesticide sorption isotherms for whole soils and soil size-separates were measured using the batch slurry equilibration method. In recent review articles, Rao and Davidson (1980), Green et al. (1980), and Wood et al. (1983) discussed in detail the various experimental methods for measuring pesticide sorption on soils as well as the quantitative expressions used for describing pesticide sorption isotherms. The reader is also referred to Koskinen (1980) for a discussion of various experimental factors that influence the sorption parameters measured by the batch method.

Aqueous solutions of the pesticides were prepared with 0.01 N $CaCl_2$ as the supporting electrolyte and spiked with sufficient amounts of ^{14}C-labeled pesticide to give ^{14}C specific activities of about 0.2 µCi/ml. The maximum initial pesticide concentration used did not exceed 50% of the aqueous solubility and the maximum equilibrium solution pesticide concentrations were generally lower than 15 µg/ml for the more soluble compounds and less than 2 µg/ml for the compounds with low solubilities.

Five ml of pesticide solution were added to 5g soil in Pyrex glass culture tubes fitted with teflon-lined screw caps and equilibrated for 24 hours by tumbling end-over-end on a shaker at 25°C. After centrifugation, the equilibrium solution concentration was assayed by liquid scintillation counting. Decrease in pesticide solution concentration was attributed to sorption on soil; in all cases preliminary studies were carried out to ascertain that pesticide losses via degradation during the 24-hr equilibration period were negligible. In selected cases, the ^{14}C-pesticide sorbed on the soils was directly measured by combusting the soil samples and recovering $^{14}CO_2$ evolved, to further ascertain that there was no pesticide loss via degradation.

The pesticide desorption isotherms were measured using the batch dilution method described by Rao et al. (1979) and Rao and Davidson (1980). Several 5g soil samples were equilibrated with 5ml pesticide solution for 24 hours as in the adsorption study. Desorption was initiated by adding different volumes of 0.01 N $CaCl_2$ solution to each tube thereby reducing the solution pesticide concentration. For each pesticide-soil combination, it was shown that solution:soil ratio did not influence the sorption isotherm parameters. The tubes, after addition of electrolyte solution, were equilibrated for another 24 hrs after which they were centrifuged and the equilibrium solution concentration was determined. From the initial adsorbed

TABLE III-1. Selected Properties of Soils Used in the Study

Soil Series	State	%OC			Clay Minerals
		W	S	F	
Cecil ls	GA	0.8	0.5	2.2	kaolinite, Fe-oxides
Grenada sl	AR	0.9	1.4	1.1	smectites
Houston cl	TX	0.8	0.5	0.8	smectites
Eustis fs	FL	1.3	0.6	9.4	quartz
Sharpsburg scl	NB	1.8	2.7	2.2	smectites
Webster scl	IA	3.3	0.9	4.3	smectites
Yolo sl	CA	0.9	0.4	1.6	smectites

W = whole soil; S = sand; F = (silt + clay)

TABLE III-2. Selected Properties of the Pesticides Used in this Study

Pesticide Name	Chemical Type	MP (°C)	Aqueous Solubility (mg/L)
Atrazine	_s_-Triazine	176	33
Cyanazine	_s_-Triazine	166	171
Metribuzin	Triazine	-	1,220
Diuron	Sub. Urea	158	42
Propachlor	Acetanilide	78	580
Carbaryl	Carbamate	142	40
Carbofuran	Carbamate	147	415
Fonofos	Org. Phos.	130	16
2,4,5-T	Phenoxy acid	154	250

concentration, and the final equilibrium solution concentration, the sorbed concentration after desorption could be calculated.

SORPTION ON WHOLE SOILS AND SOIL SIZE-SEPARATES

In order to evaluate the particle-size effect on sorption of pesticides, equilibrium isotherms for diuron and 2,4,5,-T sorption on various soil size-separates of Webster soil were measured. These two herbicides were chosen because 2,4,5-T is an ionic compound while diuron is a nonionic (though polar) compound. The soil organic carbon content (OC) of the different size-fractions of Webster soil are shown in Fig. III-1. It can be seen that OC content increases exponentially with decreasing particle-size; similar results for other soils and natural sediments were reported by Kay and Elrick (1967) and Karickhoff et al. (1979).

In Fig. III-2, the diuron adsorption isotherms for the various size-fractions of Webster soils are presented. In this figure, the pesticide amount adsorbed is expressed as mg sorbed per gram of soil organic carbon (rather than per gram of soil as is conventional). Note that when the adsorption isotherms are normalized with respect to organic carbon content, all isotherms for the whole soil and the size-separates coalesce into a single adsorption isotherm. The Freundlich coefficients, K_{oc} and N, for each fraction as well as for pooled data are summarized in Table III-3. The adsorption coefficient K increases with decreasing particle size but in proportion to increasing OC content of the finer particle-sizes. While the K-values for diuron are within a factor of 7, the K_{oc} value varies only within a factor of about 1.5 or less. Therefore, it is evident that essentially a single K_{oc} value may be used to describe diuron adsorption on Webster whole soil and all size-separates.

Similar adsorption data for 2,4,5-T, an anionic herbicide, are presented in Fig. III-3 and Table III-4. These results suggest that while the K_{oc} value of fines and whole soil was nearly the same, the K_{oc} for the sand size- fraction was approximately half that for the fines. Based upon the results presented here for diuron and 2,4,5-T herbicides and the data of earlier workers (Kay and Elrick, 1967; Karickhoff and Brown, 1978; Karickhoff et al., 1979), it may be concluded that the size-separates of a soil or sediment may be grouped into "fines" (silt + clay) and "sand" (>50 μm) and a specific K_{oc} value can then be assigned to each size-fraction.

The data presented so far have been for adsorption only. However, during a runoff event the process of interest is more likely to be desorption of pesticides from soil which is suspended in the runoff water and carried off the field. Also, once the soil particles in the runoff water reach the receiving water body (lake, river, stream, etc.) and become the bottom sediment, desorption from the sediment will be the process that determines pesticide release into the overlying water. Thus it is important to characterize pesticide desorption from whole soils and soil size-separates.

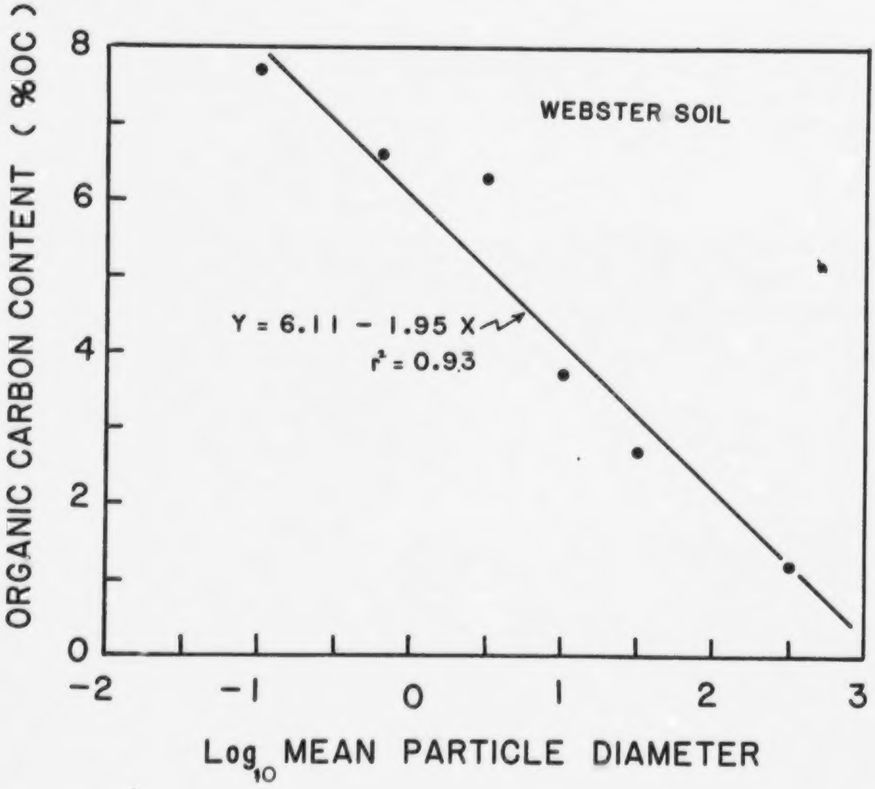

Figure III-1. Soil Organic Carbon Content as a Function of Particle-Size in Webster Soil.

TABLE III-3. Freundlich Parameters for Sorption of Diuron on Whole Soil and Size-Separates of Webster Soil

Soil Fraction	Particle-Size Range	Organic Carbon	K	K_{oc}	N
	(μm)	%			
Sand	50-2000	0.95	6.0	636	0.67
Coarse silt	20-50	2.89	16.5	570	0.77
Medium silt	5-20	3.68	32.5	884	0.59
Coarse clay	0.2-2	6.60	40.9	619	0.74
Fines	0.5-50	4.27	30.2	706	0.71
Whole soil	≧2000	3.34	24.4	733	0.75

TABLE III-4. Freundlich Parameters for Sorption of 2,4,5-T on Whole Soil and Soil Size-Separates of Webster Soil

Soil-Size Fraction	Organic Carbon	K	K_{oc}	N
	%			
Sand	0.95	0.8	86	0.82
Coarse silt	2.89	5.9	206	0.77
Medium silt	3.68	10.3	280	0.73
Coarse clay	6.60	13.5	205	0.75
Fines	4.27	8.7	204	0.80
Whole soil	3.34	6.2	186	0.78

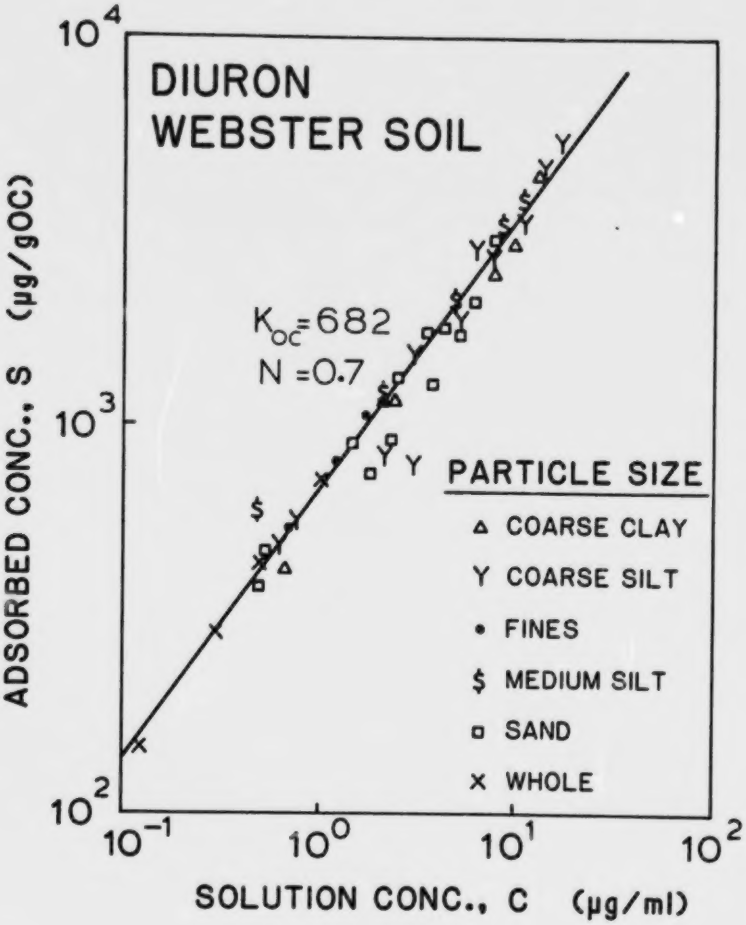

Figure III-2. Equilibrium Isotherms for Diuron Adsorption on Whole Soil and Soil Size-Separates of Webster Soil.

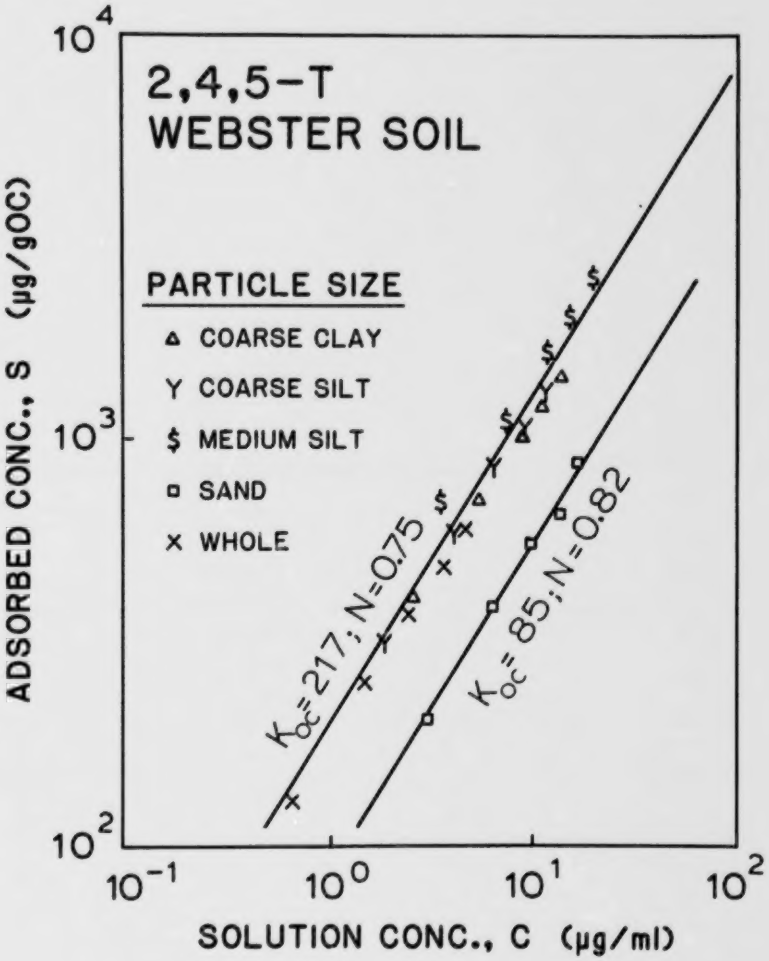

Figure III-3. Equilibrium Isotherms for 2,4,5-T Adsorption on Whole Soil and Soil Size-Separates of Webster Soil.

Isotherms for diuron desorption from Webster whole soil and various size-separates are shown in Figs. III-4 through III-7. The data presented in Fig. III-4 for whole soil suggest that diuron adsorption-desorption isotherms are nonsingular. Each of these isotherms could be described by the Freundlich equation, with the isotherm parameters being different for each desorption loop. The Freundlich N-value, (slope of the isotherm) for the desorption loops is always less than that for the adsorption isotherm and decreases with a decrease in the initial amount of pesticide adsorbed prior to desorption. A similar trend has been reported for other pesticides and soils or sediments by other workers (Swanson and Dutt, 1973; Hornsby and Davidson, 1973; Davidson and McDougal, 1973; van Genuchten et al., 1974; Peck et al., 1980).

In Fig. III-5, diuron adsorption-desorption isotherms for the fine clay fraction of Webster soil are presented. It is evident that the isotherms are singular, i.e., the same Freundlich parameters are applicable to both adsorption and desorption data. However, such is not the case for the other size-fractions of Webster soil (Figs. III-6 and III-7). In fact, the nonsingularity in sorption isotherms appears to be greater for the sand fraction when compared with silt fraction or the whole soil.

In order to quantify the extent of hysteresis (or nonsingularity) in isotherms, an index based on the Freundlich coefficients is necessary. Various authors have used different indices of nonsingularity. For example, Mukhtar (1978) used the ratio of K values, (K_d/K_a), as an index, where the subscripts a and d denote, respectively, adsorption and desorption loops. Peck et al. (1980) used the difference in N values, (N_a-N_d), as the index. More common, however, is the use of the ratio of the N values, (N_d/N_a). None of these indices have any conceptual or theoretical basis and all are empirical in nature. For reasons discussed in detail elsewhere (Nkedi-Kizza and Rao, 1983), we prefer to use the index (N_d/N_a), denoted here by β, for quantifying the extent of hysteresis in isotherms.

An examination of the data in Figs. III-4, III-6, and III-7 reveals that the β value is not unique but depends upon the initial adsorbed concentration prior to initiation of desorption. Thus, an average β-value needs to be computed. A normalization technique, described by Nkedi-Kizza and Rao (1983), was used to compute a single β value for isotherms from each size-fraction or whole soil. For each loop, the adsorbed concentrations (S) were normalized by dividing with maximum adsorbed concentration (S_M), while the solution concentrations (C) were normalized with the corresponding maximum solution concentration (C_M). The normalization is schematically presented Fig. III-8 for a single desorption loop, while measured data for silt size-fraction are shown in Fig. III-9. Note that $\beta = 1$ indicates no hysteresis (or singular isotherms), whereas $\beta > 1$ suggests nonsingularity; also, the larger the β value, the larger is the hysteresis in the system.

The β values for Webster whole soil and size-fractions estimated from normalized diuron adsorption-desorption isotherms are summarized in Table III-5. It is evident that no hysteresis exists for the fine clay $(\beta=1)$ and that the extent of hysteresis is similar for the whole soil and silt $(\beta \cong 2)$.

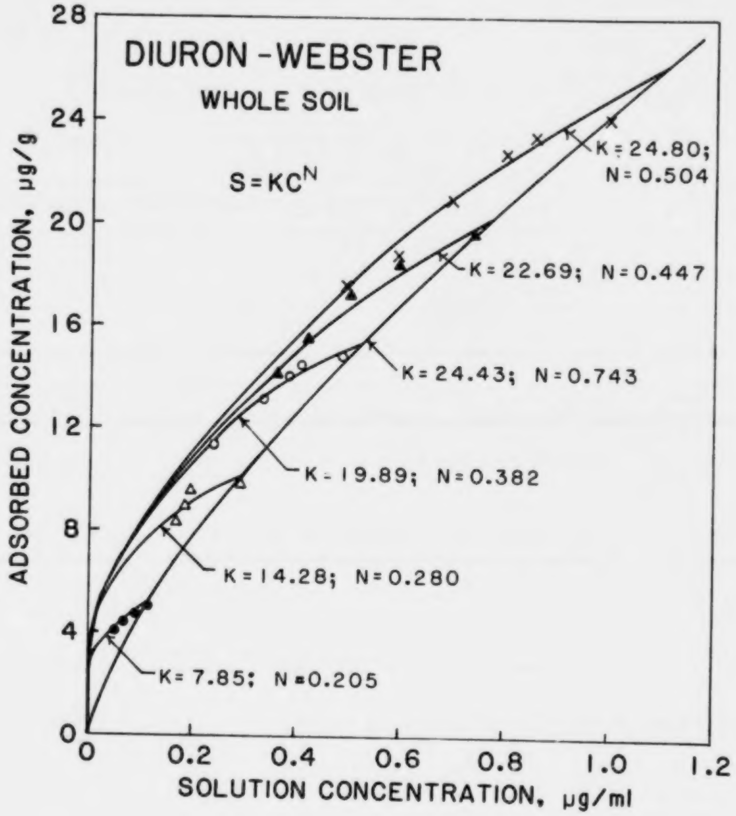

Figure III-4. Adsorption-Desorption Isotherms for Diuron Sorption on Webster Whole Soil.

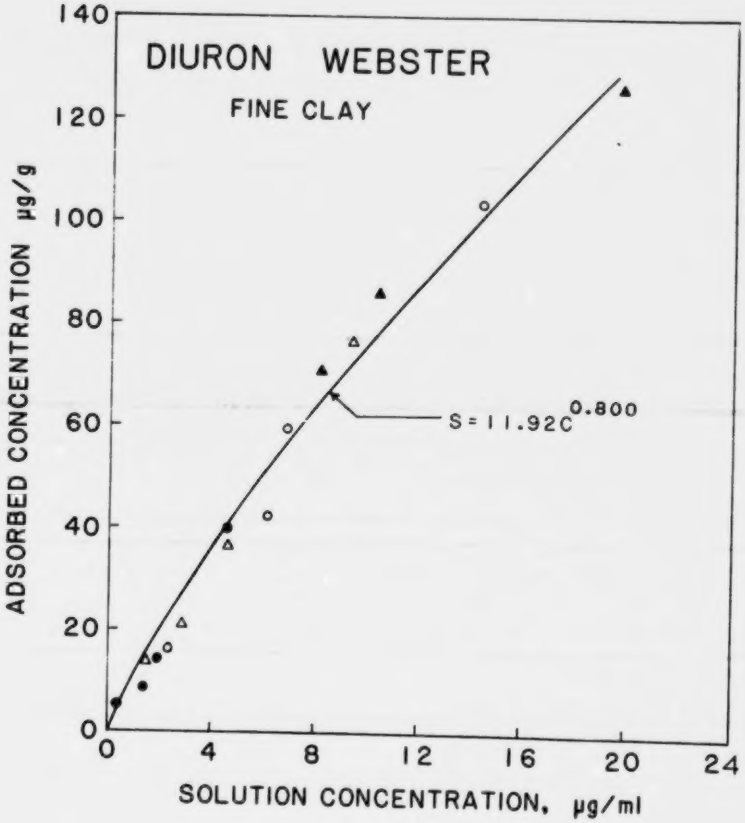

Figure III-5. Adsorption-Desorption Isotherms for Diuron Sorption on Fine Clay Fraction of Webster Soil.

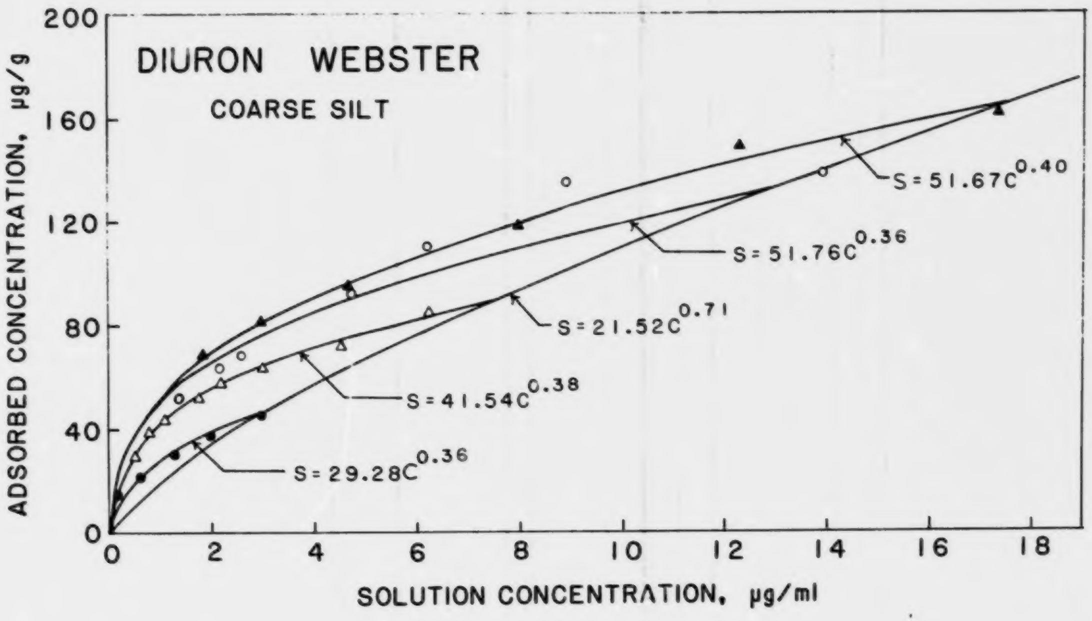

Figure III-6. Adsorption-Desorption Isotherms for Diuron Sorption on Coarse Silt Fraction of Webster Soil.

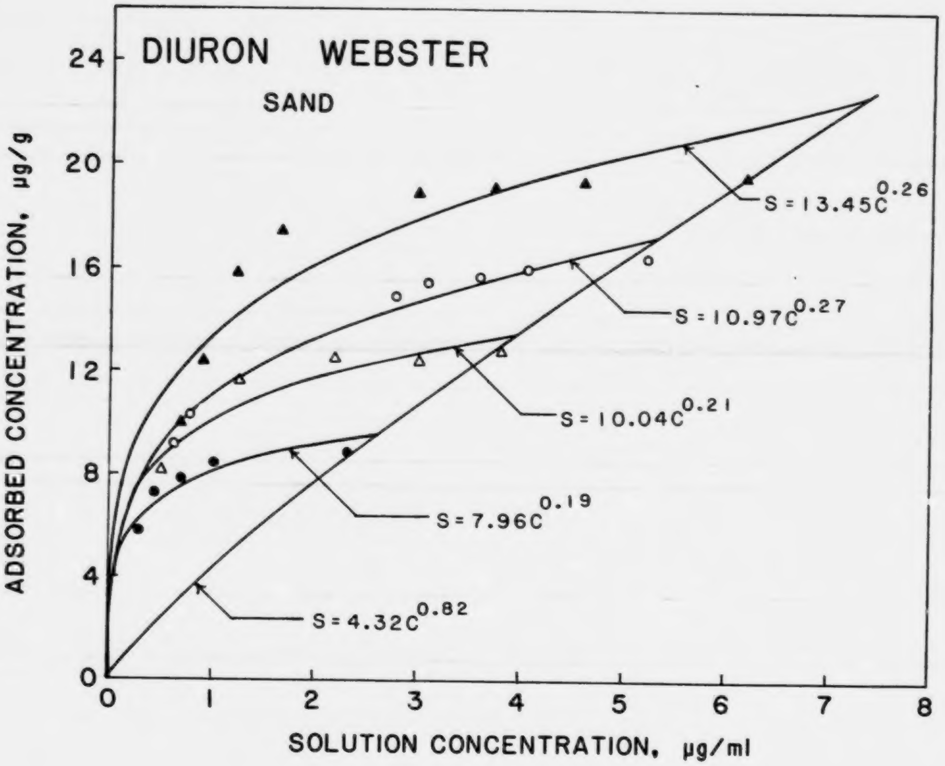

Figure III-7. Adsorption-Desorption Isotherms for Diuron Sorption on Coarse Sand Fraction of Webster Soil.

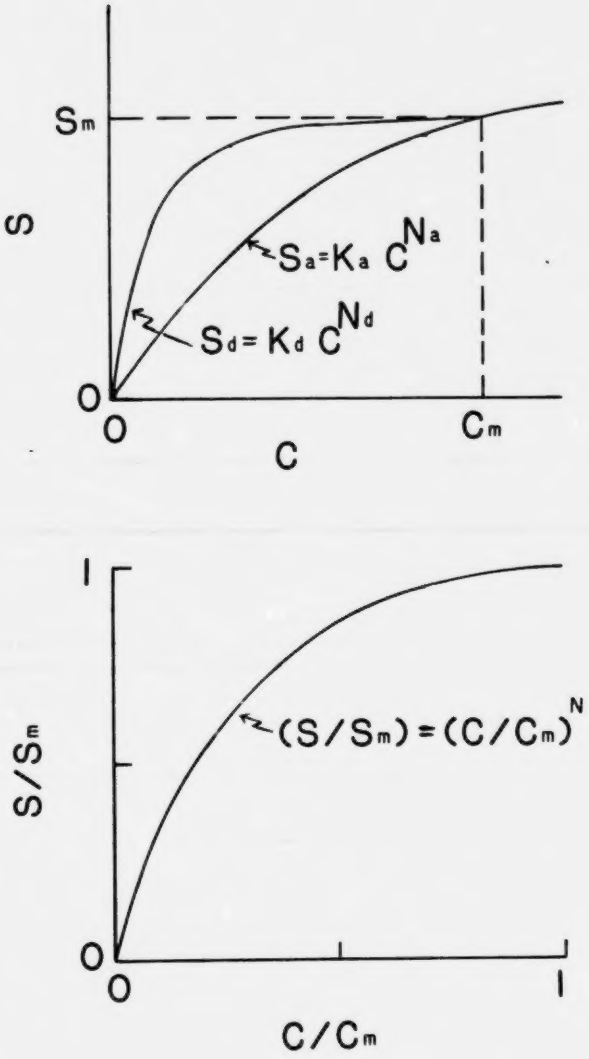
Sm
S
$S_a = K_a C^{N_a}$
$S_d = K_d C^{N_d}$
0
0
Cm
C
1
S/Sm
$(S/S_m) = (C/C_m)^N$
0
0
1
C/Cm

Figure III-8. A Schematic Diagram Showing the Procedure Used for Normalizing Adsorption-Desorption Isotherm loops.

TABLE III-5. The Values of the Hysteresis Index (β) for the Various Size-Fractions of Webster Soil

Webster Soil Fraction	$\beta = \frac{Na}{Nd}$
Fine clay	1.0
Coarse clay	2.1
Coarse silt	1.8
Sand	4.2
Whole soil	2.3

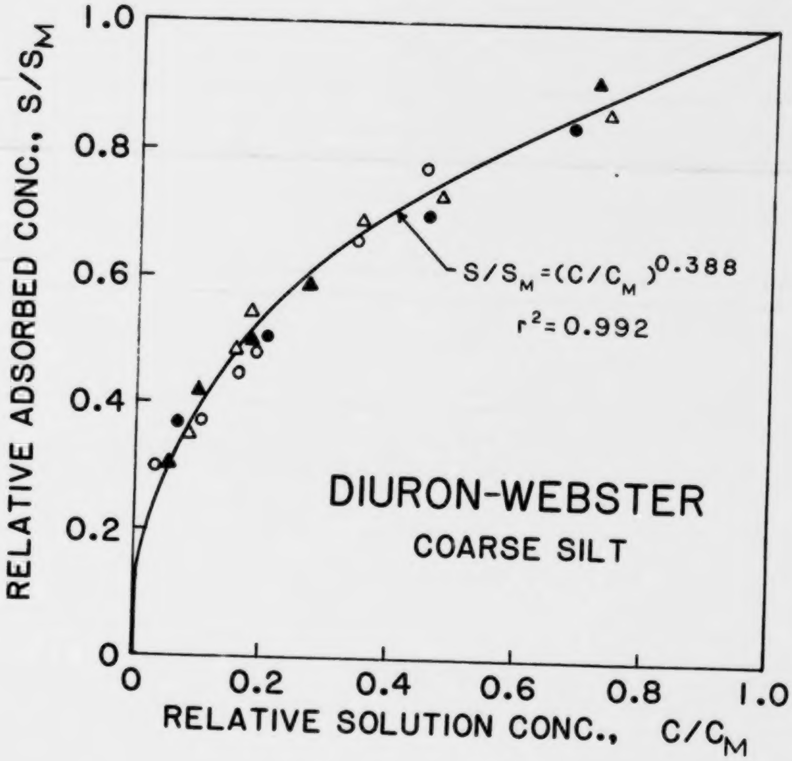

Figure III-9. Normalized Adsorption-Desorption Isotherm loops for Sorption on Coarse Silt Fraction of Webster Soil.

Also, the isotherms for the sand fraction exhibit extensive hysteresis ($\beta \cong 4$). Nkedi-Kizza and Rao (1982) showed that a large β value was also found for natural sediments that had high OC (>3%) coupled with high sand content (>10%). It may be concluded that while hysteresis may be significant for the coarser fraction, sorption isotherms may be essentially singular for finer fractions. This is especially important because it is these finer fractions that are carried off the field as sediment during runoff events.

The measured isotherms for adsorption of eight pesticides on seven whole soils and two particle-size separates from each soil (i.e., 21 isotherms for each pesticide) are shown in Figs. III-10 through III-17. In these plots, the logarithm of the amount pesticide sorbed per gram of soil organic carbon (μg/g OC) is plotted against the logarithm of the equilibrium solution concentration (μg/ml). Also, in all of these figures, the solid line represents the Freundlich equation obtained by regression for the pooled data, while the dashed lines represent "tolerance bands". These tolerance bands are defined by the isotherms whose N values are the same but the K_{oc}-values are different from the regression line by a factor of two. Finally, the total number of sorption points used in the regression analysis is indicated by n. The Freundlich coefficients, K_{oc} and N, obtained by regression of the pooled adsorption data are summarized in Table III-6.

The pooled adsorption data in Figs. III-10 through III-17 show that for each pesticide the adsorption isotherms for all soils and size-separates lie within the tolerance bands. This implies that the adsorption partition coefficient K_{oc} value can be predicted within a factor of two for any whole soil or particle-size separate. Such a variation in K_{oc} value may be found in the literature for several soils and sediments (Karickhoff and Brown, 1978; Rao and Davidson, 1980; Peck et al., 1980; Kay and Elrick, 1967).

In Figs. III-18 through III-25, the desorption data are plotted together with the adsorption data for all the soils and pesticides studied in this project. The sorption parameters, K_{oc} and N, estimated from pooled adsorption and desorption data are summarized in Table III-7. These data suggest once again that for a given pesticide the adsorption-desorption data for 7 whole soils and 2 particle-sizes for each soil lie within the designated tolerance bands. Thus, eventhough sorption isotherms for a given soil or size-fraction may be nonsingular, these pooled data examined suggest that these variations are all within a factor of two from the average K_{oc} value. Furthermore, such an average K_{oc} value from the data obtained from this study compares very well with literature-reported K_{oc} values as well as K_{oc} estimates based on solubility and melting point of the pesticide (Table III-7).

Based on these data, we may conclude that given a single (average) K_{oc} value for a pesticide and the OC enrichment factor for the sediment (due to higher content of fines), the nonpoint source loadings of pesticides may be estimated for a particular storm event.

TABLE III-6. K_{oc} and N Values for 8 Pesticides Based on Adsorption Data from 7 Whole Soils and 2 Particle-Size Separates from Each Soil.

Pesticide	Type	K_{oc}	N
Metribuzin	Herbicide	91	0.9
Propachlor	Herbicide	102	0.7
Atrazine	Herbicide	111	0.7
Cynazine	Herbicide	116	0.8
Diuron	Herbicide	534	0.6
Carbofuran	Insecticide	40	0.9
Carbaryl	Insecticide	298	0.7
Fonofos	Insecticide	770	0.7

Table III-7. K_{oc} Values Based on Pooled (Adsorption + Desorption) Data Compared with Published Average K_{oc} Values.

Pesticide	Type	This Study[*]	Lit. Avg.	Calc. Value[**]
Metribuzin	Herbicide	157	95	-
Propachlor	Herbicide	119	265	116
Atrazine	Herbicide	130	172	204
Cyanazine	Herbicide	198	190	56
Diuron	Herbicide	545	389	257
Carbofuran	Insecticide	46	29	32
Carbaryl	Insecticide	407	229	216
Fonofos	Insecticide	846	-	1400

[*] Data for whole soil, fines, and sand for 7 soils.

[**] Calculated Value; X_{sol} and MP

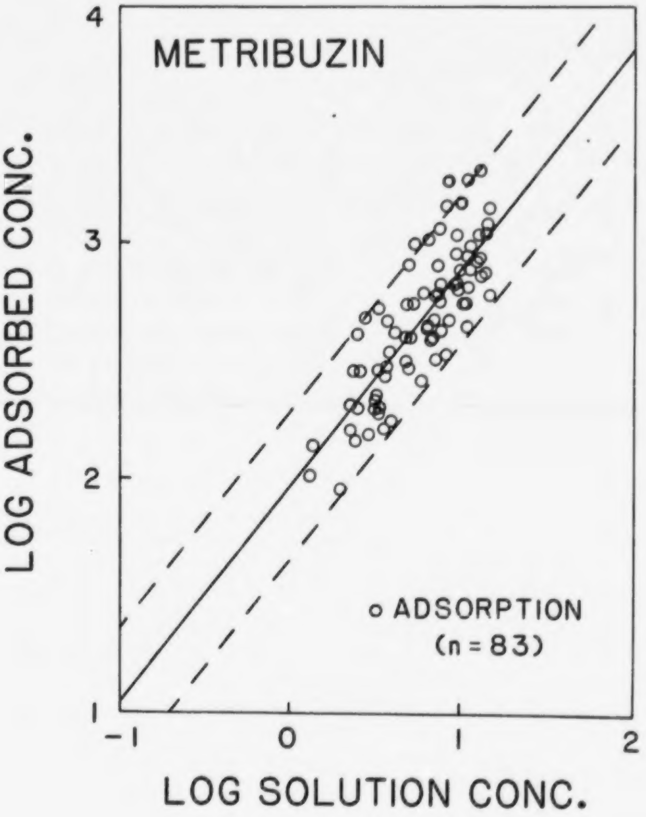

Figure III-10. Adsorption Isotherms for Sorption of Metribuzin on Whole Soils and Soil Size-Separates.

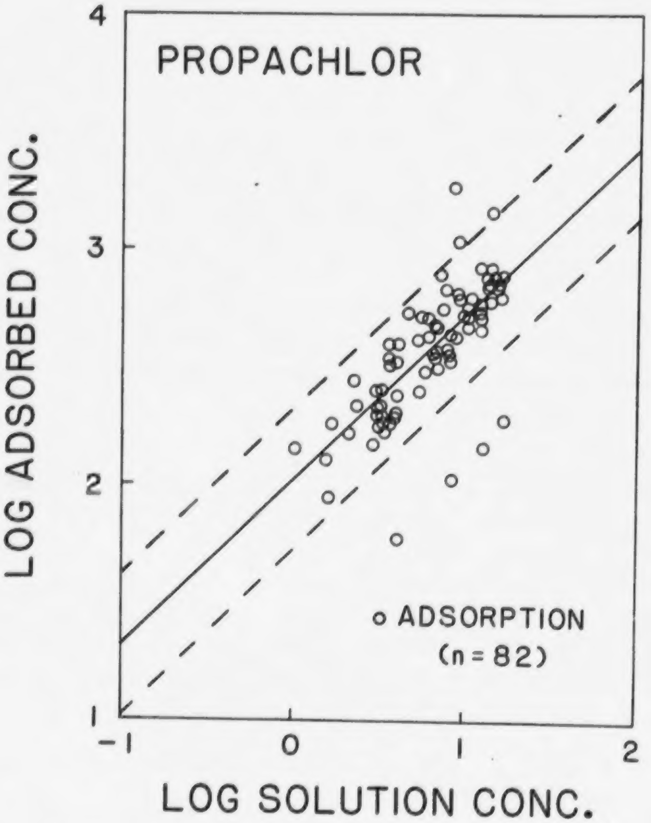

Figure III-11. Adsorption Isotherms for Sorption of Propachlor on Whole Soils and Soil Size-Separates.

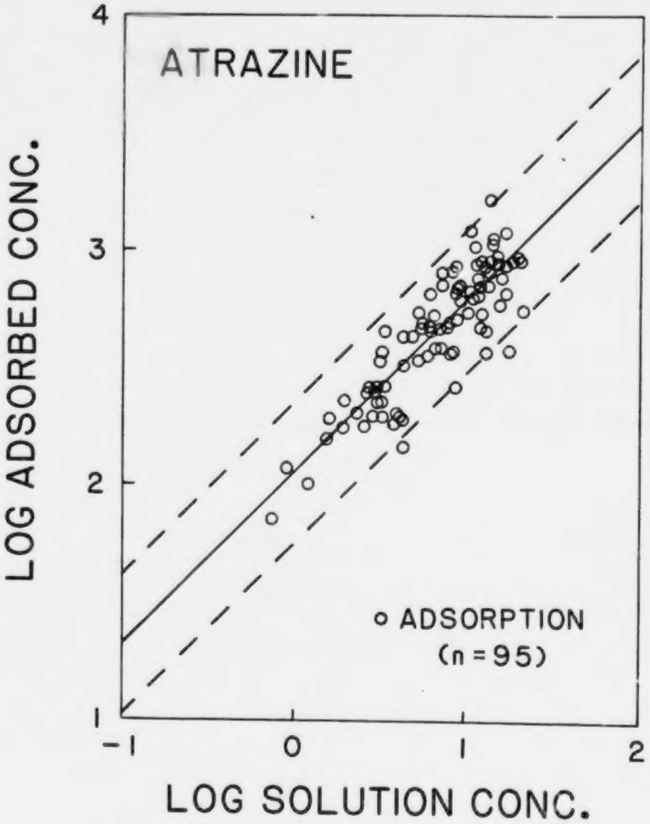

Figure III-12. Adsorption Isotherms for Sorption of Atrazine on Whole Soils and Soil Size-Separates.

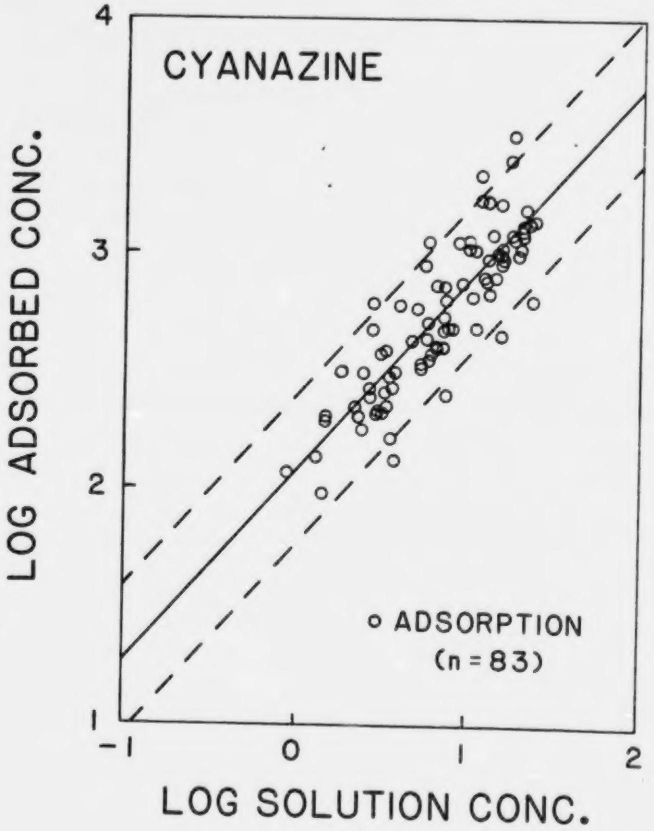

Figure III-13. Adsorption Isotherms for Sorption of Cyanazine on Whole Soils and Soil Size-Separates.

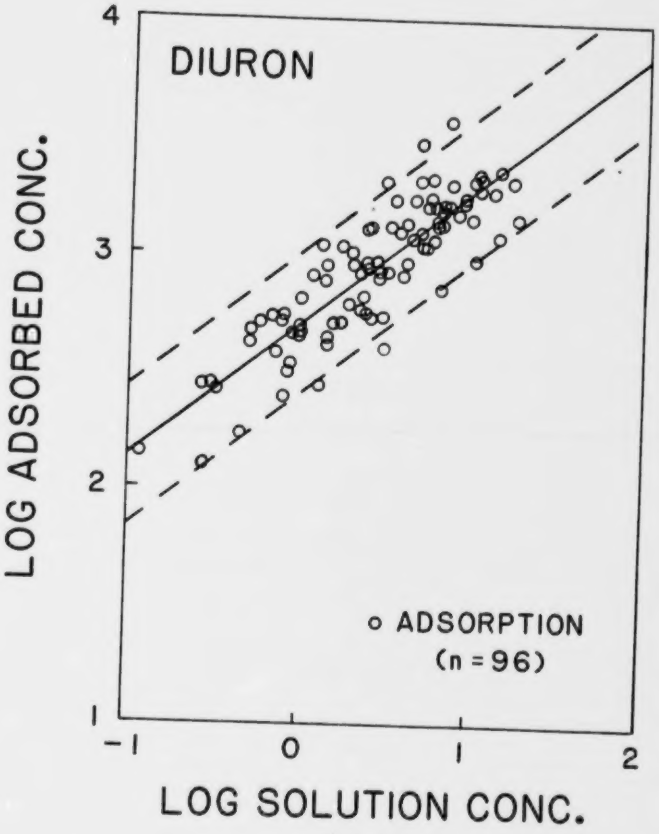

Figure III-14. Adsorption Isotherms for Sorption of Diuron on Whole Soils and Soil Size-Separates.

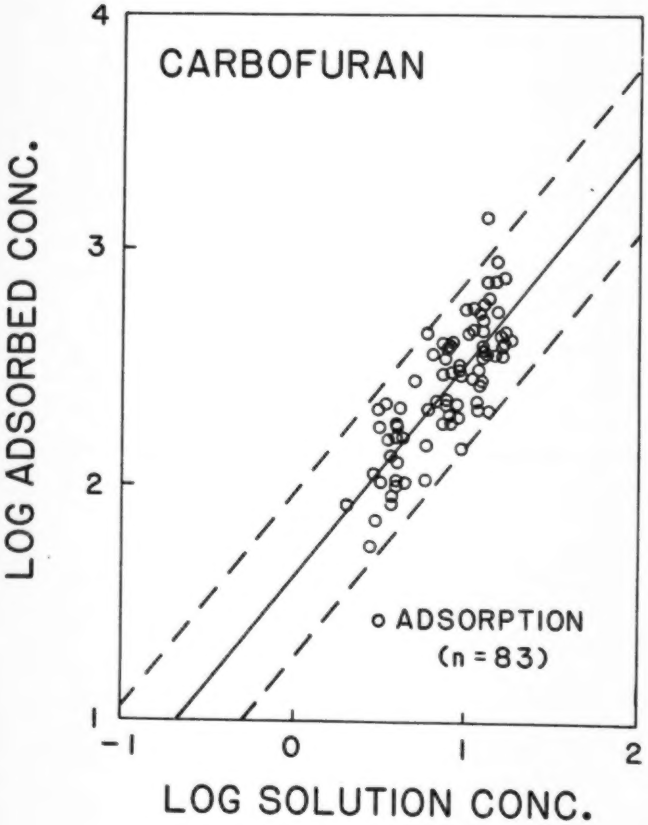

Figure III-15. Adsorption Isotherms for Sorption of Carbofuran on Whole Soils and Soil Size-Separates.

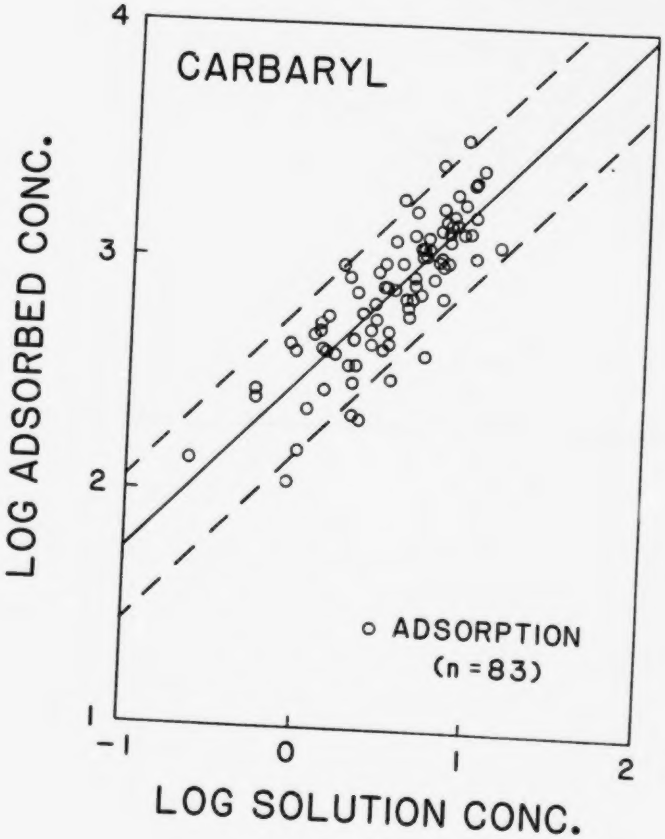

Figure III-16. Adsorption Isotherms for Sorption of Carbaryl on Whole Soils and Soil Size-Separates.

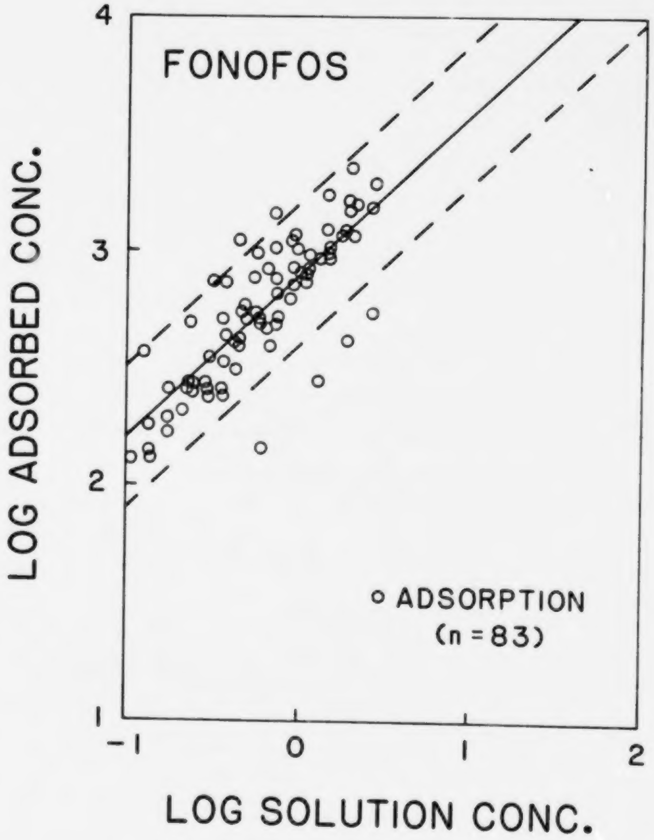

Figure III-17. Adsorption Isotherms for Sorption of Fonofos on Whole Soils and Soil Size-Separates.

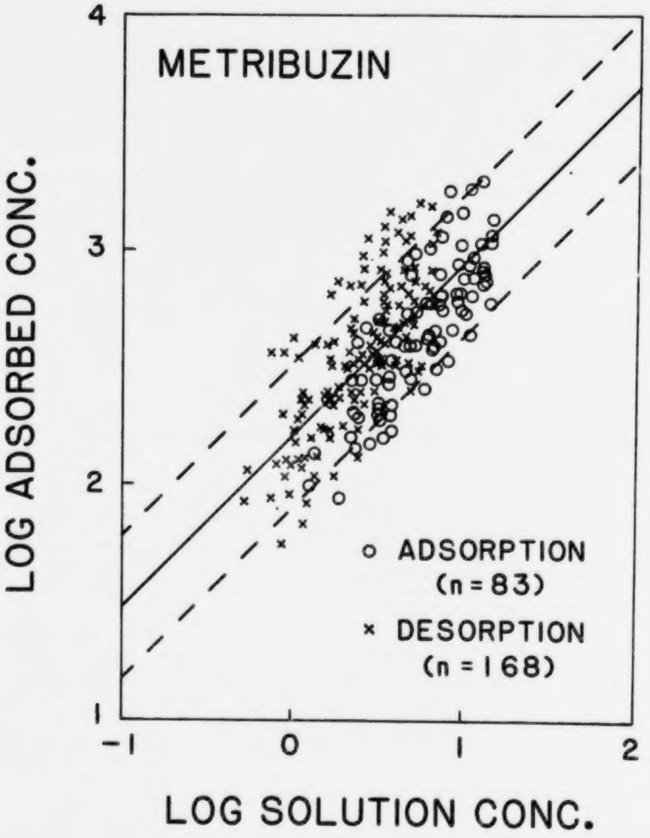

Figure III-18. Pooled Adsorption-Desorption Isotherms for Metribuzin.

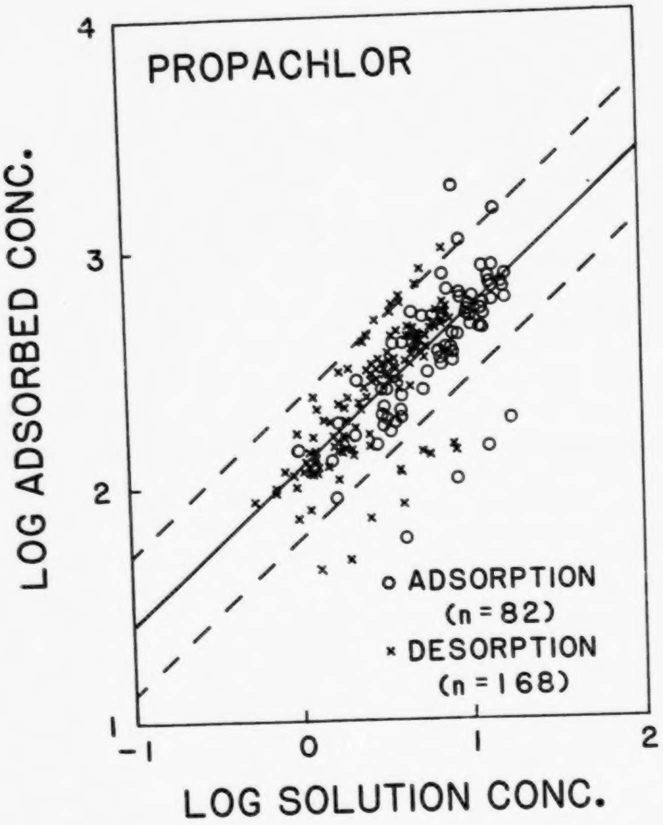

Figure III-19. Pooled Adsorption-Desorption Isotherms for Propachlor.

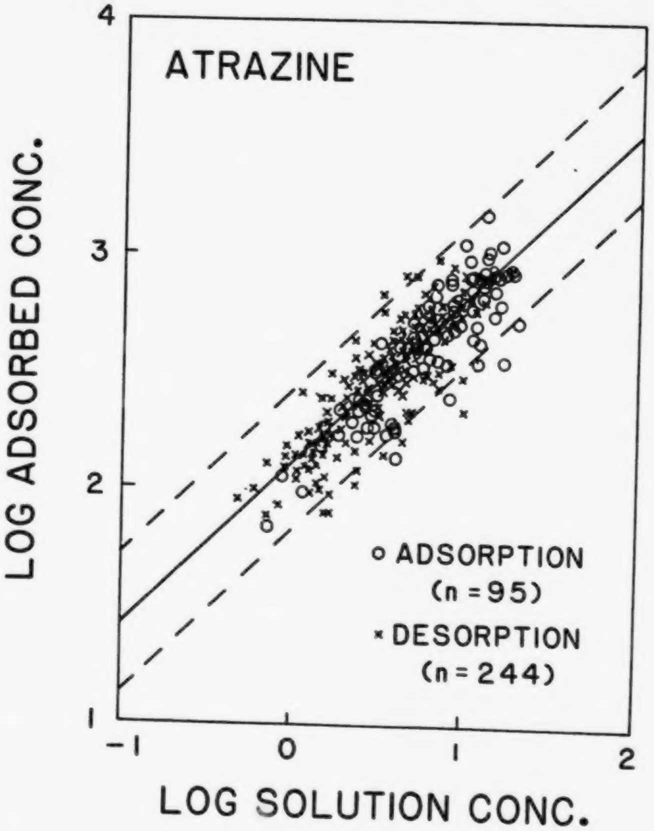

Figure III-20. Pooled Adsorption-Desorption Isotherms for Atrazine.

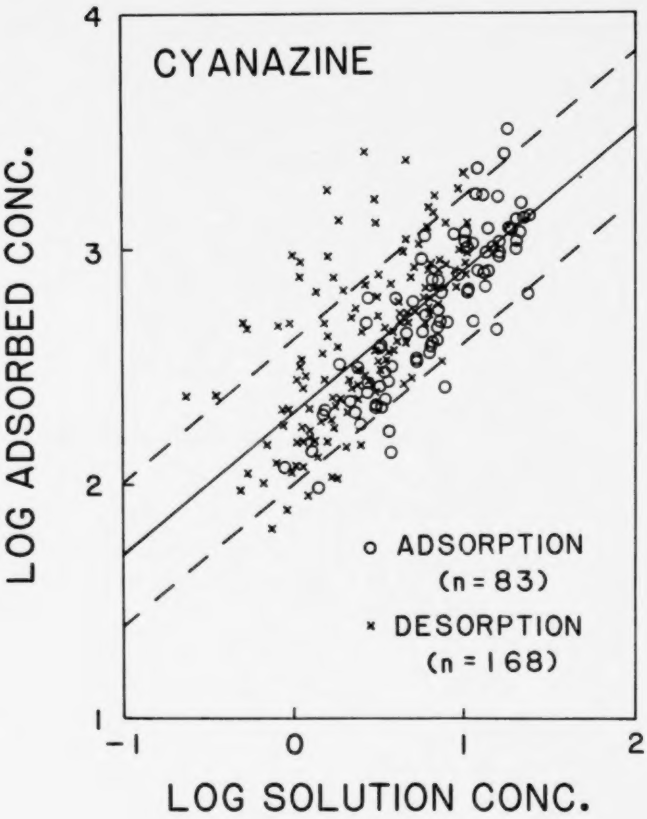

Figure III-21. Pooled Adsorption-Desorption Isotherms for Cyanazine.

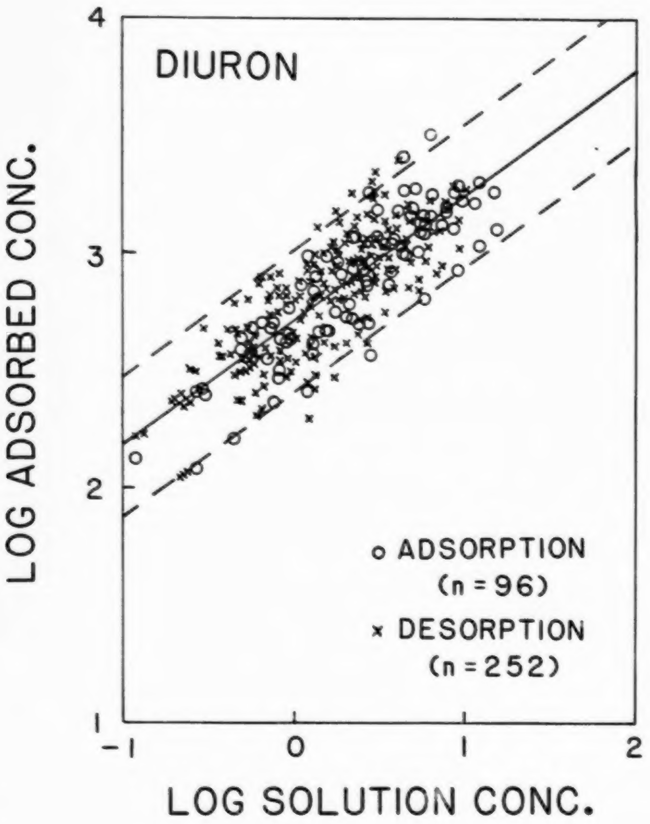

Figure III-22. Pooled Adsorption-Desorption Isotherms for Diuron.

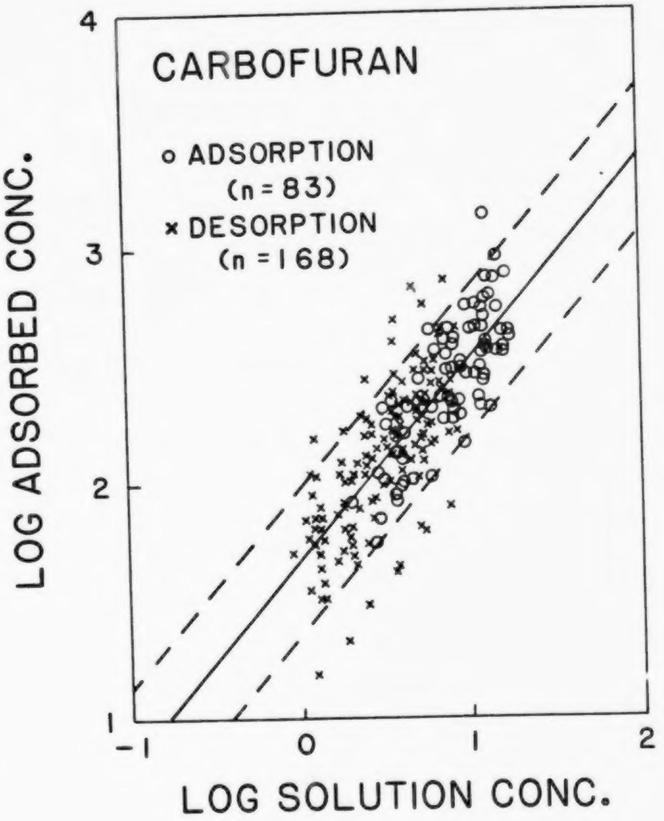

Figure III-23. Pooled Adsorption-Desorption Isotherms for Carbofuran.

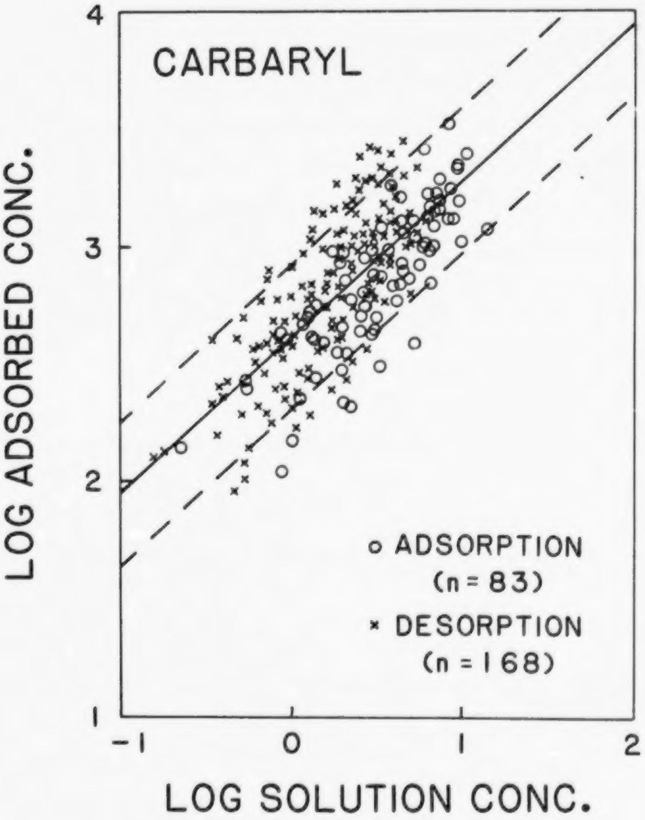

Figure III-24. Pooled Adsorption-Desorption Isotherms for Carbaryl.

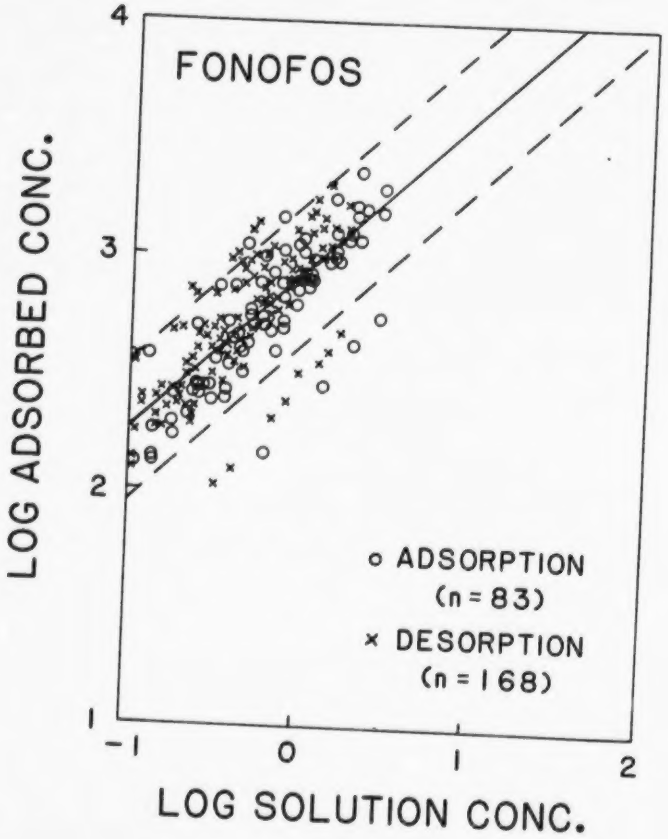

Figure III-25. Pooled Adsorption-Desorption Isotherms for Fonofos.

INDIRECT METHODS FOR ESTIMATING K_{oc}

The number of pesticides currently in use and those being tested for future use as well as the number of agricultural soil types in the U.S. alone are so large as to preclude a direct measurement of sorption isotherms for all possible soil-pesticide combinations. Economic and other considerations make attempts to acquire pesticide sorption data by direct measurements impractical if not impossible. Thus, a considerable effort has been focused in recent years on indirect estimation techniques for pesticide sorption parameters. These indirect methods utilize physical-chemical properties of the pesticide (e.g., aqueous solubility, melting point, crystal energy, and octanol-water partition coefficient) to estimate its K_{oc} value. The reader is referred to recent papers by Karickhoff and Brown (1978), Rao and Davidson (1980), Lyman (1980), Kenaga and Goring (1980), and Karickhoff (1981) for a detailed discussion of these indirect methods.

Here we will examine three relationships presented recently by Karickhoff (1981):

$$\log K_{oc} = -0.921 \log X_{sol} - 0.00953\,(MP-25) - 1.405 \qquad [1]$$

$$\log K_{oc} = -0.594 \log X_{sol} - 0.197 \qquad [2]$$

$$\log K_{oc} = \log K_{ow} - 0.346 \qquad [3]$$

In Eqs. (1) and (2), X_{sol} is the mole fraction aqueous solubility, MP is the melting point in °C, and K_{ow} is the octanol-water partition coefficient. The melting point (MP) value in Eq. (1) is set equal to 25°C for compounds that are liquids at 25°C, thus eliminating the second term in Eq. (1). Karickhoff (1981) obtained the coefficients in Eqs. (1)-(3) by regressing measured K_{oc} values with K_{ow}, X_{sol}, and MP values for five polycyclic hydrophobic compounds (benzene, napthalane, phenanthrene, anthracene, and pyrene).

The K_{oc} values estimated by Eqs. (1)-(3) are compared in Table III-8 with average measured K_{oc} values for several pesticides reported in the literature. It is evident from Table III-8 that for 15 of the 21 pesticides listed (71%), Eq. (1) provided K_{oc} estimates within a factor of three; such deviations are not uncommon for K_{oc} values reported in the literature for a wide range of soils and sediments (Rao and Davidson, 1980; Kenaga and Goring, 1980). The data presented in Table III-8 also indicate that K_{oc} values estimated by Eqs. (2) and (3) are within a factor of three for about only half of the pesticides. Thus, the use of Eq. (1) for estimating K_{oc} is preferred. The reader is referred to the paper by Karickhoff (1981) for a detailed discussion of the possible reasons for the discrepancies between measured and calculated K_{oc} values listed in Table III-8.

As indicated by Eq. (3) K_{oc} values are directly correlated with octanol water partition coefficient (K_{ow}) values. Generally, K_{ow} values have been measured using direct liquid-liquid partitioning (Karickhoff and Brown, 1979). Recently, a high-pressure liquid chromatographic (HPLC) method for estimating K_{ow} values has been proposed (Vieth et al., 1978; Ellgehausen et al., 1981). In this method the retention times of pesticides and other

Table III-8. Comparision of Calculated and Measured K_{oc} Values for a Number of Pesticides (Adapted from Karickhoff, 1981).

Pesticide	Measured K_{oc}	Calculated K_{oc} Eq. (1)	Eq. (2)	Eq. (3)
Atrazine	172	204	1,288	87
Propazine	207	309	2,951	355
Simazine	158	339	4,571	59
Trietazine	549	229	1,778	912
Ipazine	1,161	1,259	1,230	3,548
Cyanazine	190	56	513	71
Carbaryl	229	316	1,096	263
Carbofuran	29	32	288	48
Chlorpropham	589	1,333	668	468
Malathion	1,778	1,950	676	316
Parathion	7,161	8,913	1,778	2,630
Methyl Parathion	7,079	2,951	1,047	851
Chlorpyrifos	13,490	74,131	912	10,552
Diuron	389	257	1,148	100
Fenuron	34	6	68	4
Linuron	841	631	85	163
Monolinuron	237	120	229	16
Monuron	135	33	380	25
Fluometuron	174	105	741	9
Terbacil	46	11	209	32
Bromacil	72	22	214	43

organics in a reverse-phase C-18 column, eluted isocratically with methanol water mixture, are correlated with measured K_{ow} values. Using selected compounds as standards to obtain a calibration curve, the K_{oc} values for other compounds can be estimated by measuring the retention time in a C-18 column. McCall et al. (1980) and Volk et al. (1983) have extended this HPLC method to estimate K_{oc} values directly. In Fig. III-26 the data of Volk et al. (1981) are shown, where the logarithms of K_{ow} or K_{oc} are plotted against logarithms of normalized retention times (k') for several organic chemicals. The HPLC column retention times (k) were normalized by dividing with k_o, the retention time for acetone. The K_{ow} and K_{oc} values used in Fig. 1 were either measured in our laboratory or were taken from the literature. The data presented in Figs. III-26 can be described well by the two regression equations given below:

$$\ln K_{ow} = 3.391 + 1.446 \ln k' \; ; \; r^2 = 0.77 \qquad [4]$$

$$\ln K_{oc} = 3.594 + 1.618 \ln k' \; ; \; r^2 = 0.78 \qquad [5]$$

Volk et al. (1983) also evaluated the reproducibility of the HPLC method by having three operators determine the retention times at least ten times each for a mixture of five organic compounds (acetone, benzene, bromobenzene, biphenol, and p,p-DDE). These results indicated that the coefficients of variation (CV) for k' values determined by a single operator were less than 1% in all cases, while the CV values for inter-operator variability in all cases were less than 0.4%. Thus, retention times by the HPLC method could be determined reproducibily by various operators following a given protocol.

ENVIRONMENTAL SIGNIFICANCE

In the foregoing section of this Chapter, we have examined the retention of pesticides in soils and soil size-separates. In this section we will briefly examine one aspect of the environmental significance of nonpoint source pesticide loadings from croplands. When dealing with pesticide losses from croplands two types of measurement are relevant: 1) the total amount of pesticide that is lost during a runoff event, and 2) the pesticide concentration in the runoff (solution- and sediment-associated). Based on an extensive literature review, Wauchope (1978) concluded that in most cases the total losses of weakly-sorbed pesticides were generally less than 0.5% of that applied; the herbicide paraquat and organochlorine insecticides, which are strongly-sorbed, were the exceptions. Wauchope (1978), Smith et al. (1978), and Wauchope and Leonard (1980), among others, noted that single- event pesticide losses decreased exponentially with time after pesticide application. However, losses of up to 10% of the applied pesticide were reported during "catastrophic" events, which are the high rainfall events that occur shortly after pesticide application. This is when most of the applied pesticide is readily available for runoff in the surface mixing zone (0-1 cm surface depth).

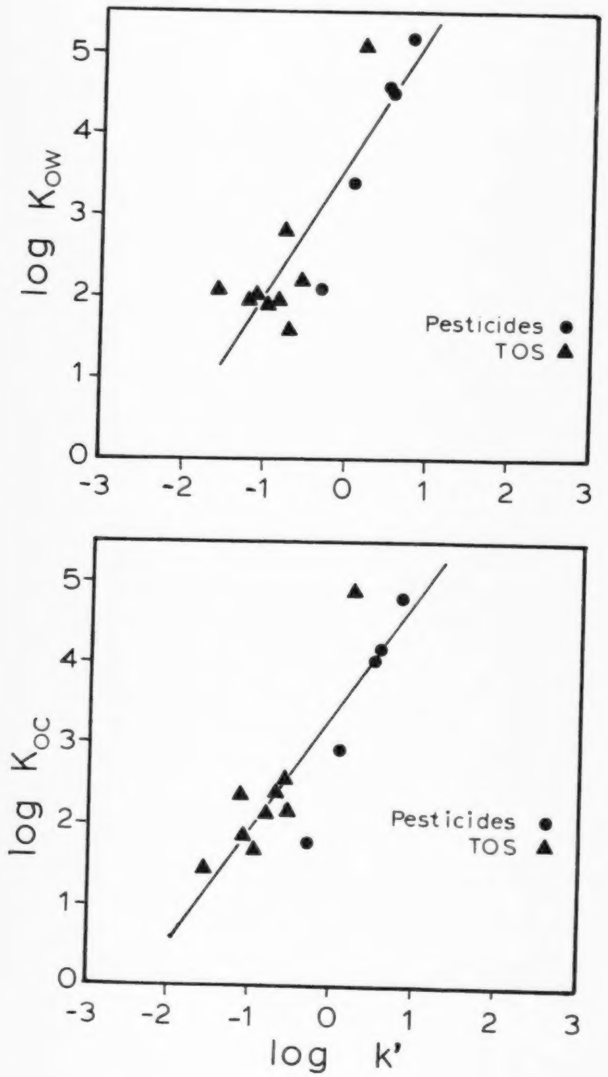

Figure III-26. Relationship between log of adjusted retention time (k') and log of K_{ow} or log of K_{oc} values. TOS refers to toxic organic substances.

Table III-9. A Comparison of the Observed Edge-of-Field Concentrations and LC_{50} Values for Several Pesticides (Compiled Using Literature Data).

Pesticide	Measured concentration[*] (μg/L)	LC_{50}[**] (μg/L)
I. Herbicides:		
Atrazine	120 - 4,700	13,000
Cyanazine	101 - 275	-
Diuron	74	760,000
2,4-D[§]	8 - 4,210	-
2,4,5-T[§]	117 - 3,300	-
Simazine	300	-
Prometryne	90 - 150	≅1,000
Picloram	2 - 5,210	-
Trifluralin	0.5 - 15	30
II. Insecticides:		
Carbaryl	248	≅1,000
Carbofuran	1,002 - 1,403	-
DDT	67 - 725	2
Diazinon	-	30
Fonofos	10 - 60	30
Malathion	-	19

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[*] The range in values was based on data presented by Wauchope and Leonard (1980). Concentrations shown are bulk (sediment plus water) concentrations.

[**] Values were compiled by Davidson (1980), unpublished report.

[§] Includes acid and salt forms.

Total edge-of-field pesticide losses may be important in determining the long-term impacts of nonpoint source loadings on the quality of the receiving water bodies. On the other hand, pesticide concentrations in the runoff for a given storm event may be more important in determining short-term environmental impacts (e.g., fish kills). In Table III-9, a comparison is made between observed edge-of-field concentrations and LC_{50} values for several insecticides and herbicides. The measured concentrations shown in Table III-9 are the bulk concentrations (i.e., sediment- plus water-associated) and are from the literature review of Wauchope and Leonard (1980). For weakly-sorbed pesticides, the bulk concentrations are essentially equal to solution-phase concentrations because most (≧ 95%) of the pesticide is carried in the water- phase. For strongly-sorbed pesticides, the bulk concentrations are primarily sediment-associated. The results in Table III-9 indicate that the measured herbicide concentrations in the runoff are generally lower than the LC_{50} values whereas the insecticide concentrations in the runoff might approach or even exceed the LC_{50} values. It should not be concluded, however, that when runoff concentrations are greater than the LC_{50} there will be an immediate harmful environmental impact. Mayeux et al. (1983) observed a rapid dilution of picloram in a large stream during rising stage of flow after introduction of the herbicide near the upper end. They attributed the decreases in picloram concentrations to hydrodynamic mixing (diffusion and dispersion) of water during stream flow and dilution with uncontaminated water entering downstream. Thus, dilution of the pesticide in the receiving water bodies (streams, rivers, and lakes) as well as pesticide fate and dynamics in the water body itself must be considered before a proper assessment of the adverse environmental impact can be made.

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CHAPTER IV

DEGRADATION AND BINDING OF PESTICIDES IN SOILS

L. T. Ou, P.S.C. Rao, and W.B. Wheeler

INTRODUCTION

Knowledge of degradation rates for pesticides in terrestrial and aquatic environments is necessary in order to estimate their residual lives and for predicting their fate in the environment. Two types of degradation rates are often reported in the literature, i.e. the disappearance rate of the parent chemical and the mineralization rate. In order to determine the amounts of pesticide residues in soils, plants, sediments, and water, organic solvents are generally used for extraction. The amount of pesticide found in the solvent extracts is used to estimate the parent chemical disappearance rate. This type of degradation rate is called the solvent-extractable parent chemical disappearance rate. On the other hand, mineralization rate represents the total degradation of the pesticide to inorganic forms such as CO_2, H_2O, Cl^-, NO_3^-, NO_2^-, NH_3, SO_4^{-2}, etc. Mineralization rates are not reported as commonly as the parent chemical disappearance rates because of the general unavailability and expense of ^{14}C-labeled pesticides.

Mineralization rate is generally lower than the rate of parent chemical disappearance. Accumulation of degradation products, formation of bound residues and assimilation into microbial mass account for the discrepancy between these two rates. Substantial amounts of the pesticides could become nonextractable and form bound residues in soils (Katan et al., 1976, Lichtenstein et al., 1977; McCall et al., 1981). Degradation products, especially oxidation and reduction products, may possess toxicity similar to the parent chemical. On the other hand, the chemical may be assimilated into the microbial mass through biochemical pathways, and result in a loss of the biological toxicity. Therefore, the parent chemical disappearance rate may overestimate the true degradation rate, while the mineralization rate may underestimate the true degradation rate. True degradation rate is being defined here as the rate at which a pesticide is degraded to nontoxic metabolites.

In this study, the rates of solvent-extractable parent chemical disappearance and mineralization for selected pesticides were evaluated in six U.S. soils maintained at various levels of soil-water tensions and temperatures. Attempts were made to correlate the two types of degradation rates with soil temperature and soil-water tension as well as with other key soil factors including pH, CEC, organic carbon, clay content, and microbial populations. The formation of metabolites and nonextractable bound residues during aerobic incubation was also investigated.

EFFECT OF ENVIRONMENTAL FACTORS

Pesticides in soils are subject to biological, chemical and photochemical degradation. Of these processes, biological degradation is the most important in degrading the pesticides. The rate of degradation of a pesticide in soil in agroecosystems is related to its chemical structure, to its distribution in the soil profile and to the physicochemical and biological environments of the soil. Chemical degradation and photodecomposition may also contribute to pesticide dissipation in soils. Because soil below surface is inaccessible to sunlight, the role of photodecomposition may be generally insignificant in field soils. Pesticide losses due to volatilization, runoff, leaching and uptake by micro- and macro-organisms do not generally cause alteration of the pesticide's chemical structure and simply involve the transfer of the pesticide among the various environmental compartments.

Microbial activity in soil is influenced by several soil and environmental factors. As a result pesticide degradation rate is also affected by these factors. A number of soil and environment factors including soil water content, soil temperature, soil pH, organic matter content, clay content, CEC, Eh and oxygen tension are considered to influence soil microbial activity. Of these factors, soil moisture, Eh and oxygen tension are interrelated; increase in soil moisture results in a decrease of Eh and oxygen tension. Wilson and Griffin (1975) demonstrated that soil respiration was adversely affected by soil-water tension at levels higher than 3 bars. Anderson (1981) showed that soil-water content significantly influenced the microbial mass and its activity. The mineralization rate of herbicide diallate expressed as mg herbicide degraded per unit mass of microorganisms in soil increased as soil-water content increased. Raney (1965) reported that a close association existed between the soil-water content of a soil and its adsorption capacity. Increase in temperature results in increase in metabolic activity which may in turn lead to an increase in pesticide degradation rate. Walker and coworkers (Smith and Walker, 1977; Walker, 1974; 1976 a,b; Walker and Smith, 1979) considered soil-water and temperature to be the two most important environmental factors influencing pesticide degradation rates in soils. They reported that the solvent-extractable parent chemical-disappearance rate for several herbicides (2,4,5-T, simazine, prometryne, napropramide, metamitron, trifluralin, metribuzin, atrazine, pronamide, linuron and clorthaldimethyl) correlated reasonably well with soil temperature and soil-water content under laboratory conditions. Furthermore, they used these results to simulate the persistence of the herbicides under field conditions with a reasonable degree of success.

MATERIALS AND METHODS

Soils

Six U.S. soils used in this study were: Cecil loamy sand (Typic Hapludult) (Georgia), Webster sandy clay loam (Typic Haplaquoll) (Iowa), Grenada silt loam (Glassic Fragiudalfs) (Arkansas), Sharpsburg silty clay loam (Typic Agiudolls) (Nebraska), Yolo silt loam (Typic Xerorthrents) (California) and Houston clay loam (Typic Chromuderts) (Texas). Selected properties of these soils are shown in Table IV-1. The soil-water contents and the corresponding soil-water tensions are listed in Table IV-2.

Pesticides

Table IV-3 lists the common and chemical names of the nine pesticides and their ^{14}C-label positions used in this study. The purities of the ^{14}C- pesticides, checked by TLC-radioautographic assay and liquid scintillation counting, were all found to exceed 98%. The unlabeled pesticides were either analytical grade (≧ 99% purity) or technical grade (≧ 95% purity). ^{14}C- pesticide stock solutions were prepared by dissolving the chemical in pesticide-grade methanol to give a specific activity of 10 μCi/ml. The concentration of unlabeled pesticide stock solutions was 1000 μg/ml in methanol. The pesticide solutions were stored in dark at 4°C.

Soil treatments

Five hundred g (oven-dry weight basis) of soil were placed in a 2000 ml glass bottle and 5 ml of ^{14}C-labeled pesticide stock solution (10 μCi/ml) were added along with an appropriate amount of the unlabeled pesticide stock solution. This resulted in a pesticide concentration and ^{14}C-activity in the soil of 10 μg/g (except for methyl parathion) and 0.1 μCi/g, respectively; the methyl parathion concentration in soils was 25 μg/g. After the organic solvent had evaporated from the soil under an aerated hood, the soil was mixed thoroughly. A 10g portion of the pesticide-treated soil was withdrawn for immediate determination of ^{14}C-activity in the soil by combusting in a Packard Tri-Carb sample oxidizer. The CO_2, including $^{14}CO_2$, evolved was trapped in a liquid scintillation solution cocktail containing an organic amine and ^{14}C-activity was determined by liquid scintillation counting.

Extractable- and nonextractable-^{14}C-activity

Ten g of the pesticide-treated soils were transferred to a culture tube (50 ml capacity) with a teflon-lined screw cap. An appropriate amount of distilled H_2O was added to each tube to establish a soil-water tension of 0.1, 0.33, 1 or 15 bars. After mixing, the tubes were incubated at 15°, 25°, 27° or 35°C. The caps were removed at weekly intervals and at the same time the weights of the tubes were checked. Distilled H_2O was added as needed to the tubes to compensate for moisture loss, if any.

A solvent mixture consisting of equal volumes of acetone, methanol and benzene was used to extract pesticide residues and their metabolites from

TABLE IV-1. Selected Characteristics of the Soils Used in the Study.

Soil	pH	Oganic carbon	Mechanical analysis sand	silt	clay	CEC	Microbiota bacteria	fungi
		%	------%	-----		meq/100g	------cfu/g*	--------
Webster	7.3	3.9	55	20	25	21.8	3.9×10^7	6.2×10^5
Cecil	5.6	0.9	77	17	6	3.4	1.7×10^7	3.9×10^5
Sharpsburg	5.6	1.8	6	59	35	27.0	7.9×10^7	6.2×10^5
Grenada	5.7	0.9	27	66	7	5.2	5.6×10^7	1.8×10^5
Houston	7.7	0.8	21	49	30	27.7	5.3×10^7	4.8×10^5
Yolo	6.9	1.4	20	58	22	16.0	5.6×10^7	4.4×10^5

*cfu/g - colony forming units per g of oven dry soil.

TABLE IV-2. Water contents* of the six soils at various soil-water tensions.

Soil	SOIL-WATER TENSION Air dry	0.1 bar	0.33 bar	1 bar	15 bars
Webster	5.4	32.8	27.1	15.0	10.2
Cecil	0.5	13.5	9.5	4.3	2.5
Sharpsburg	3.7	40.3	31.8	19.6	10.2
Grenada	0.6	29.2	22.0	13.5	4.2
Houston	5.9	42.0	33.8	23.8	14.0
Yolo	2.9	34.5	27.5	16.0	8.0

* Gravimetric basis; g water/100 g oven-dry soil.

TABLE IV-3. The Common Names and the Chemical Names of the Pesticides Used in This Study, and Their ^{14}C-label Positions and Specific Activities.

Common name	Chemical name	^{14}C Label positions	Specific activity (mCi/mM)
Atrazine	2-Chloro-4-(ethylamino)-6-(isopropylamino)-S-triazine	1,3,5 positions	8.3
Carbaryl	1-naphthyl methylcarbamate	2,4,6 positions	20.7
Carbofuran	2,3-dihydro-2,2-dimethyl-7-benzofuranyl-N-methylcarbamate	uniformly ring labeled	6.2
2,4-D	2,4-dichlorophenoxyacetic acid	uniformly ring labeled	9.2
Diuron	3-(3,4-dichlorophenyl)-1,1-dimethylurea	uniformly ring labeled	12.2
Fonofos	0-ethyl S-phenyl ethylphosphorodithioate	uniformly ring labeled	16.7
Methoxychlor	2,2-bis(p-methoxyphenyl)-1,1,1-trichloroethane	uniformly ring labeled	4.3
Methyl parathion	0,0-dimethyl 0-p-nitrophenyl phosphorothioate	uniformly ring labeled	1.8
Propachlor	2-chloro-N-isopropylacetanilide	uniformly ring labeled	9
2,4,5-T	2,4,5-trichloroacetic acid	uniformly ring labeled	4.5

TABLE IV-4. TLC Solvent Systems Used for Identification of Parent Chemicals and Metabolites.

Pesticide	Solvent system v/v
Atrazine	Hexane/acetone, 4:1
Carbaryl	Ether/hexane, 4:1
Carbofuran	Hexane/acetone, 7:3
2,4-D	i. n-butanol/acetic acid/H_2O, 8:1:1 ii. $CHCl_3$/acetic acid, 40:1^2
Fonofos	Hexane/$CHCl_3$/methanol, 7:2:1
Methyl parathion	i. Hexane/$CHCl_3$/methanol, 7:2:1 ii. Acetone/benzene/H_2O, 50:10:7
Propachlor	Benzene/methanol, 4:1

soils. For extraction of 2,4-D residues, the solvent mixture was acidified with 10 ml of conc. HCl per 1000 ml of the solvent mixture. A 25 ml aliquot of the solvent mixture was added to a culture tube containing 10 g of the pesticide-treated soil. The tubes were shaken mechanically for 30 minutes, followed by vacuum filtration through Whatman No. 42 filter papers. After four successive extractions, the extracts were combined and the ^{14}C-activity in the extracts were determined by liquid scintillation counting.

The ^{14}C-activity remaining in the extracted soils was determined by combusting soil sample in a Packard Tri-Carb sample oxidizer, and the evolved $^{14}CO_2$ was trapped in a scintillation solution containing an organic amine. The ^{14}C-activity associated with CO_2 was quantified by liquid scintillation counting.

Metabolites

The volume of the extracts was reduced to 1 ml by evaporating under a stream of N_2. The parent chemical and its metabolites in the concentrated extracts (except for the methyl parathion extracts) were separated on commercial silica gel-G TLC plates. The developing solvent systems for pesticides used in this study are listed in Table IV-4. After development, the plates were air-dried and each plate was placed on a Kodak 20-screen X-ray film for 3-4 weeks for autoradiographic analysis. The R_f value of each radioactive area was compared with the R_f values of standard chemicals which were suspected to be the metabolites. Each radioactive area on the plates was scrapped and transferred to a scintillation vial, and the amount ^{14}C-activity was quantified by liquid scintillation counting.

The concentrated methyl parathion extracts were partitioned into water and hexane phases by shaking with a 6:4 H_2/hexane mixture for 20 minutes. The two phases were separated from each other and ^{14}C-activity in each phase was counted. Methyl parathion and nonpolar metabolites would be partitioned into the hexane phase, while the polar metabolites would remain in the H_2O phase. The water and hexane extracts were then concentrated to 1 ml. TLC-autoradiographical analysis was performed as described previously.

Mineralization Rates

To study the rates of $^{14}CO_2$ evolution from ^{14}C-pesticide treated soils, 10 g of the pesticide-treated soil were placed in a 250 ml Erlenmeyer flask which had contained 90 g of the untreated soils, unlabeled pesticide and 5 ml of distilled H_2O. The final concentration of the pesticide in soil was 10 μg/g (except for methyl parathion) and containing radioactivity of 1 μCi. The final concentration of methyl parathion was 25 μg/g of soil. An appropriate volume of distilled H_2O was added to bring soil-water tension to 0.1 or 0.33 bar. After mixing, the flasks were connected to a plexiglas manifold and CO_2-free water-saturated air was continually passed through the flask at a rate of 10 ml per minute. The air leaving each incubation flask was bubbled through a standardized KOH solution (0.1-0.2N) to absorb the evolved CO_2 except for the methyl parathion and trifluralin treated soil samples. The air passed through these samples was first bubbled through ethylene glycol to trap volatilized chemicals, and then through KOH solution. The KOH solutions were changed frequently to prevent saturation with CO_2. The ethylene glycol was changed biweekly. Radioactivity in the KOH and ethylene glycol was determined by liquid scintillation counting. The flasks were incubated at 25° ± 2°C.

DEGRADATION AND METABOLISM RATES

Atrazine

Mineralization rates--

Based on the data collected during 60 days of aerobic incubation, the half-lives of uniformly ring-labeled ^{14}C-atrazine in six soils (Cecil, Webster, Grenada, Sharpsburg, Houston and Yolo) were all over 1000 days. The half-lives were obtained based on the first-order kinetics. Less than 2% of applied ^{14}C-atrazine in the six soils was mineralized to $^{14}CO_2$ in 60 days. Doyle et al. (1978) reported that 14% of applied ^{14}C-ethyl side chain of atrazine in a silt loamy soil was mineralized in 60 days of aerobic incubation. Obviously microbial disruption of the ring structure is much slower than the disruption of side chains.

Carbaryl

Mineralization rates--

Mineralization rates of uniformly ring-labeled ^{14}C-carbaryl varied greatly from soil to soil (Table IV-5). The half-life for carbaryl in the 0.1 bar Houston soil was 23 days, while the half-life for 0.33 bar Sharpsburg soil was 665 days. The half-life in the 0.1 bar soil was significantly shorter than in the 0.33 bar soil except for the Webster soil. The half-life in the 0.1 bar Webster soil was significantly longer than in the 0.33 bar treatment. The average half-life in the six soils was 274 ± 234 days. It is not clear that repeated applications of carbaryl would accelerate degradation in soils as the case of 2,4-D and MCPA (Loos, 1975). No information was available regarding to the history of carbaryl application in these soils.

Disappearance rates--

No significant influence of soil-water tension (0.1 to 15 bars) on the disappearance rates of extractable ^{14}C-activity in soils incubated at 25°C was observed with the exception of the 15-bar Yolo soil (Table IV-6). The disappearance rate in the 15-bar Yolo soil was significantly lower than the other three lower soil-water tension treatments. The half-lives in the Yolo soil maintained at soil-water tension levels of 0.1, 0.33 and 1 bar were significantly shorter than the other three soils maintained at the same levels of soil-water tension. The Yolo soil has a history of repeated annual applications of 2,4-D and it was observed that 2,4-D was degraded more rapidly than the soils which did not have a history of receiving 2,4-D.

TABLE IV-5. Mineralization Rate Constants (k_1) and Half-Lives ($t_{½}$) of Carbaryl in Soils.

Soil-water tension bars	k_1 days^{-1} $\times 10^3$	$t_{½}$ - days	r2
		Cecil	
0.1	2.29	303	.992
0.33	1.02	681	.996
		Webster	
0.1	1.80	386	.978
0.33	2.61	266	.966
		Grenada	
0.1	6.02	115	.962
0.33	4.02	172	.980
		Sharpsburg	
0.1	1.44	482	.982
0.33	1.04	665	.982
		Houston	
0.1	29.80	23	.861
0.33	15.40	45	.990
		Yolo	
0.1	12.60	55	.920
0.33	7.27	95	.859

TABLE IV-6. Rate Constants (k_1) and Half Lives ($t_{\frac{1}{2}}$) for Solvent Extractable ^{14}C-Activity Disappearance in Soils Treated with ^{14}C-Carbaryl.

Soil-water tension bars	Temp. °C	k_1 days^{-1} x10^3	$t_{\frac{1}{2}}$ days	r2	k_1 days^{-1} x10^3	$t_{\frac{1}{2}}$ days	r2
			Cecil			**Webster**	
0.1	25	2.57	27	.921	1.90	37	.725
0.33	25	1.96	35	.755	1.86	37	.759
1	25	2.02	34	.765	1.85	37	.770
15	25	1.62	43	.799	1.99	35	.703
			Sharpsburg			**Yolo**	
0.1	25	2.25	31	.823	6.89	10	.943
0.33	25	2.08	33	.812	3.84	18	.806
1	25	2.01	35	.865	4.48	16	.964
15	25	1.74	40	.945	1.49	46	.947

This suggested that the enhancement of 2,4-D degradation may have a synergistic effect on carbaryl degradation.

Bound residues--

Substantial amounts of applied radioactivity in soils formed nonextractable ^{14}C-residues after 28 days of aerobic incubation (Table IV-7). The formation of nonextractable ^{14}C in the 15-bar soils was generally slower but the difference was not great.

Carbofuran

Mineralization rates--

The mineralization rates of uniformly-ring labeled ^{14}C-carbofuran in soils incubated at 27°C and 0.1 and 0.33 bar of soil-water tension under aerobic incubation approximated first-order kinetics as indicated by the coefficients of determination (r^2) (Table IV-8). Mineralization rates (k_1) for soils maintained at 0.1 bar of soil-water tension were generally higher than for soils maintained at 0.33 bar except for the Houston soil. Mineralization rates for the Sharpsburg soil were at least two times smaller than those for the other soils. The average half-life of carbofuran in all treatments was 397 ± 239 days. If the Sharpsburg soil was excluded, the average half life was 298 ± 63 days. There was no statistical correlation between mineralization rate and number of aerobic bacteria, number of aerobic fungi, soil pH, organic matter content, clay content, or CEC.

Metabolites--

Carbofuran (I) and four metabolites 3-hydroxycarbofuran (II), 3-ketocarbofuran (III), carbofuran phenol (IV) and 3-ketocarbofuran phenol (V) were detected in the carbofuran-treated Cecil and Webster soils at the completion of the 28-day aerobic incubation period (Table IV-9). Carbofuran phenol was detected only in the Cecil soil maintained at 0.1 and 15 bars. The metabolites accounted for no more than 5% of total extractable ^{14}C-activity with the exception of the 0.33 bar Cecil soil in which the metabolites accounted for 7% of the total extractable ^{14}C-activity in the 0.33 bar Cecil soil. 3- ketocarbofuran phenol appeared to be the major metabolite. No carbofuran phenol was detected in any of the treatments at the 14th day of aerobic incubation and less than 4.5% of total extractable ^{14}C-activity was associated with the three metabolites. Unlike aerobic soils, carbofuran phenol was the major metabolite in the anoxic soils (Venkateswarlu and Sethunathan, 1978, 1979). The proposed aerobic degradation pathways for carbofuran in soils are shown in Fig. IV-1.

Disappearance rates--

Table IV-10 lists the solvent extractable ^{14}C-activity disappearance rate constants (k_1) and half lives ($t_{1/2}$) of carbofuran in the six soils aerobically incubated at temperatures of 15°, 27°, and 35°C, and maintained at soil-water tension of 0.1, 0.33, 1 and 15 bars. Most of the rates

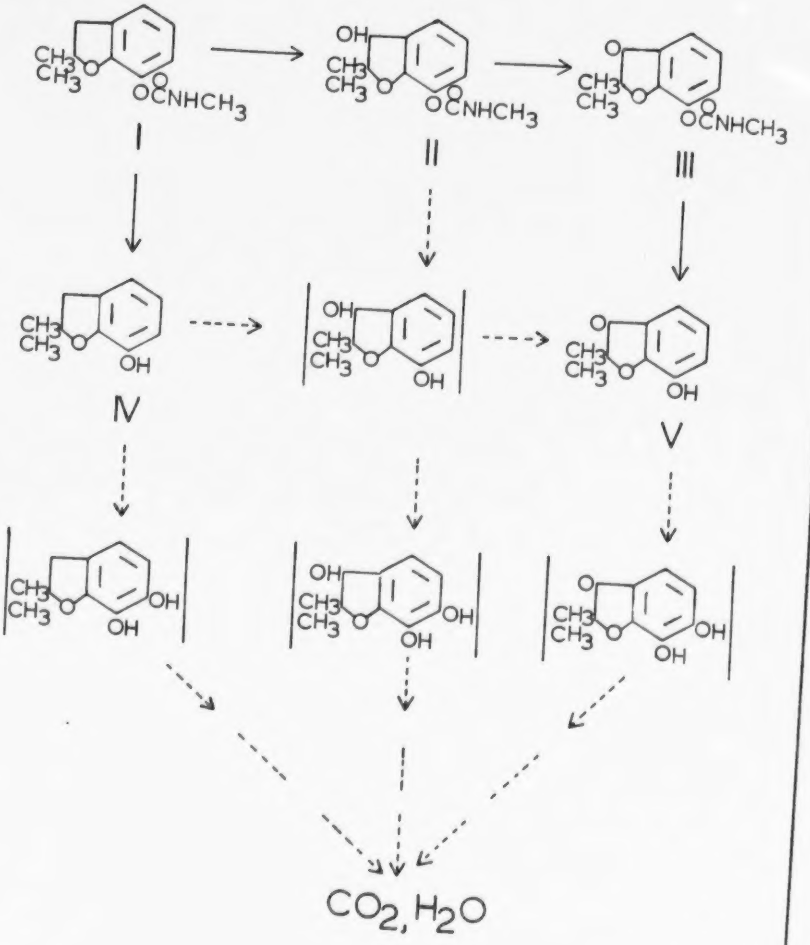
I
II
III
IV
V
CO_2, H_2O

Figure IV-1. The proposed aerobic degradation pathways of carbofuran in soils.

TABLE IV-7. Distribution of Applied ^{14}C in Soils Treated with ^{14}C-Carbaryl After 28 Days of Aerobic Incubation at 25°C.

Soil-water tension bars	Extractable ^{14}C %	Nonextractable ^{14}C %	Extractable ^{14}C %	Nonextractable ^{14}C %
	Cecil		**Webster**	
0.1	44.3	41.0	50.9	43.9
0.33	51.2	45.1	52.0	43.9
1	49.2	38.5	51.2	40.9
15	58.4	30.2	48.5	52.1
	Sharpsburg		**Yolo**	
0.1	48.8	37.1	15.3	36.6
0.33	51.9	36.2	23.6	38.1
1	53.5	33.8	29.1	36.8
15	59.8	31.8	63.7	27.4

TABLE IV-8. First-Order Kinetics Rate Constants (k_1) and Half-Lives ($t_{½}$) for Carbofuran Mineralization in Soils Incubated at 27°C.

Soil	Soil-water tension	k_1	$t_{½}$	r^2
	bar	$days^{-1} \times 10^4$	days	
Cecil	0.1	24.8	279	.996
	0.33	19.8	350	.988
Webster	0.1	32.8	216	.999
	0.33	29.4	236	.994
Grenada	0.1	25.3	273	.999
	0.33	15.7	442	.992
Sharpsburg	0.1	8.3	839	.994
	0.33	7.3	944	.998
Yolo	0.1	25.6	271	.996
	0.33	23.5	295	.996
Houston	0.1	21.8	317	.990
	0.33	23.0	302	.992

TABLE IV-9. Radioactive Distribution of Uniformly Ring Labeled ^{14}C-Carbofuran in the Solvent Extracts from the Cecil and Webster Soils at the 28th Day of Aerobic incubation.

Soil-water tension	Carbofuran	3-hydroxy-carbofuran	3-keto-carbofuran	Carbofuran phenol	3-keto-carbofuran phenol
bars			% ^{14}C-activity		
			Cecil		
0.1	96.5	0.4	0.3	1.5	1.3
0.33	93.0	1.7	1.7	0	3.6
1	97.7	1.0	0.8	0	1.5
15	96.8	0.6	0.4	1.3	0.8
			Webster		
0.1	95.6	1.1	0.6	0	2.7
0.33	95.8	1.3	0.9	0	2.0
1	96.9	1.0	0.5	0	1.6
15	97.1	1.4	0.4	0	1.1

TABLE IV-10. First-Order Rate Constants (k_1) and Half Lives ($t_{1/2}$) for Disappearance of Extractable ^{14}C in Soils Treated with Carbofuran.

Soil-water tension	Temperature	k_1	$t_{1/2}$	r^2	k_1	$t_{1/2}$	r^2
bars	°C	$days^{-1} x10^3$	days		$days^{-1} x10^3$	days	
			Cecil			**Webster**	
0.1	15	5.4	129	.893	13.8	50	.872
0.1	27	21.8	32	.999	50.5	14	.997
0.1	35	27.0	26	.971	43.9	16	.934
0.33	15	5.0	139	.885	12.5	55	.917
0.33	27	21.6	32	.998	41.9	17	.988
0.33	35	25.7	27	.973	38.2	18	.952
1	15	5.1	135	.835	11.5	60	.926
1	27	15.2	46	.988	30.0	22	.994
1	35	20.0	35	.964	34.2	20	.975
15	15	2.7	261	.859	6.5	107	.772
15	27	8.3	84	.667	15.6	45	.833
15	35	3.8	185	.811	14.8	47	.904
			Grenada			**Sharpsburg**	
0.1	27	15.3	45	.889	13.2	53	.972
0.1	35	24.8	28	.992	7.7	91	.963
0.33	27	17.6	39	.971	11.0	64	.978
0.33	35	22.8	30	.946	7.1	97	.942
1	27	15.5	45	.964	10.7	65	.976
1	35	21.0	33	.980	4.9	143	.673
15	27	13.8	50	.810	3.9	176	.611
15	35	9.5	73	.852	3.1	227	.446
			Houston			**Yolo**	
0.1	27	37.9	18	.985	23.9	29	.962
0.1	35	125.0	5	.941	-	-	-
0.33	27	29.6	24	.988	20.8	33	.941
0.33	35	122.0	6	.990	-	-	-
1	27	30.1	23	.974	13.8	50	.875
1	35	98.6	7	.982	-	-	-
15	27	6.4	109	.653	4.5	155	.448
15	35	33.0	21	.987	-	-	-

approximated first-order kinetics as indicated by determination coefficients (r^2). In this study only the solvent extractable ^{14}C-activity disappearance rates are reported. Since the great majority of ^{14}C-activity in the solvent extracts was the parent chemical carbofuran, the difference between the solvent extractable parent chemical disappearance rate and the solvent extractable ^{14}C-activity disappearance rate was insignificant. For example, the solvent extractable carbofuran disappearance rate constants in the Cecil and Webster soils maintained at 27°C and 0.33 bar were 2.19×10^{-2} and 4.19×10^{-2} days^{-1} compared with solvent extractable ^{14}C-activity disappearance rate constants 2.12×10^{-2} and 4.29×10^{-2} days^{-1}.

An increase in temperature from 15° to 27°C had a greater influence on the solvent extractable ^{14}C-activity disappearance rate in the Cecil and Webster soils than an increase from 27°C to 35°C. The Arrhenius activation energy (ΔE_a) for a temperature increase from 15° to 27° ranged from 12.5 to 20.9 Kcal/mole (Table IV-11). The ΔE_a values for a temperature increase from 27° to 35°C were much smaller and ranged from 6.0 to -18.1 Kcal/mole. The small positive or negative ΔE_a indicated that the degradation rate was near maximum at 35°C or had reached maximum between 27° and 35°C. ΔE_a values for a temperature increase from 27° to 35° in the Grenada and Sharpsburg soils were either small positive or negative values with the exception of the 0.1 bar Grenada soil. The ΔE_a values for a temperature increase from 27° to 35°C in the Houston soil were all very high.

The logarithm of k_1 values for the solvent extractable ^{14}C-activity disappearance rates in the Cecil and Webster soils correlated well with the logarithm of soil-water tension (C) (Fig. IV-2) when soil temperature was maintained at a constant level (15°, 27° or 35°C). The regression lines for 27° and 35° were close to each other which agrees with the conclusion that the temperature for maximum degradation was between 27° and 35°C. Thus, microbial degradation appears to be the major factor controlling the disappearance of carbofuran from soils, although chemical hydrolysis may play a role in the hydrolysis of carbofuran to carbofuran phenol (Getzin, 1973).

The relationship between the k_1 values of solvent extractable ^{14}C-activity disappearance rate and the product of temperature (T,°C) and moisture content (θ,T) for Cecil and Webster soils together was considered using the empirical equation developed by Smith and Walker (1977):

$$k_1 = aT\theta + b \qquad \text{(IV-1)}$$

where a and b are constants. It was assumed that the degradation rate reached a maximum at 27°C. Equation IV-1 for Cecil and Webster soils was found to be (Fig. IV-3):

$$k_1 = 0.0000488\ T\theta + 0.0036943 \qquad \text{(IV-2)}$$

The determination coefficient (r^2) for equation 2 was 0.78. Considering the empirical nature of Equation IV-2, the fact that a single regression line describes the data for two soils is probably fortuitous; hence, no significance should be attached to equation IV-2 unless similar relationship can be established for other soils. The r^2 was poor (<0.5) when soil-water tension (ψ) instead of θ was considered. Also poor correlation (r^2<0.5) was found

TABLE IV-11. The Arrhenius Activation Energy Constants (ΔE_a) of Carbofuran Degradation in Soils.

Soil-water tension	Cecil	Webster	Grenada	Sharpsburg	Houston
bars	--------------------------Kcal/mole----------------------				
			15° - 27°C		
0.1	20.0	18.5	-	-	-
0.33	20.9	17.2	-	-	-
1	15.6	14.1	-	-	-
15	16.2	12.5	-	-	-
			27° - 35°C		
0.1	5.0	-3.3	11.1	-12.4	27.5
0.33	2.5	-2.0	5.9	-9.6	32.5
1	6.0	2.3	6.9	-18.1	27.3
15	-18.1	-1.1	-8.6	-5.8	37.7

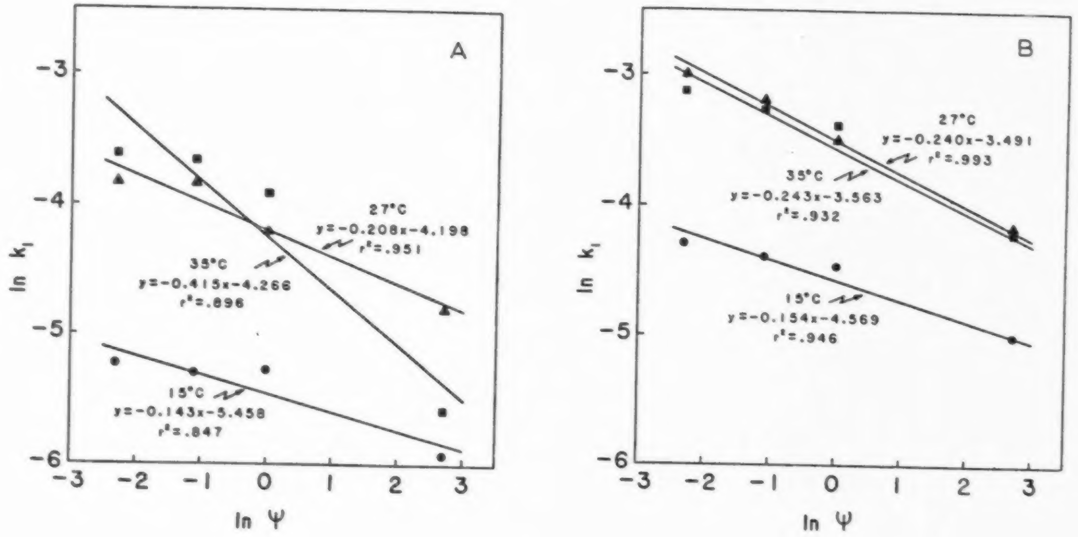

Figure IV-2. The relationship between the rate constant (k_1) for solvent-extractable 14C-activity disappearance and soil-water tension (ψ) in Cecil and Webster soils maintained at a constant temperature of 15, 27, or 35 C. (A) Cecil soil; (B) Webster soil.

when the data from all six soils were considered together. However, it should be noted that k_1 values were not available for temperature below 27°C from the Grenada, Sharpsburg, Houston and Yolo soils. A stepwise multiple regression analysis was employed to correlate k_1 values for the six soils with key soil factors including soil pH, organic matter content, clay content, CEC, total aerobic microbial population, total aerobic bacterial population, soil temperature, and soil-water tension (or soil-water content). The r^2 values for all factors together and each individual factor were low (<0.3). No correlation with soil properties was found for decomposition of herbicides 2,4-D and 2,4,5-T in six soils (McCall et al., 1981).

Bound residues--

The formation of nonextractable ^{14}C-activity in soils maintained at various levels of soil-water tensions generally followed the trend of the 0.33 bar soil treatment (Fig. IV-4). Nonextractable ^{14}C-activity in soils, in most cases, increased with the incubation time. The amount of nonextractable ^{14}C-activity formed at the completion of incubation (28 days) varied greatly with soil type, soil temperature and soil-water tension (Table IV-12). Percentages of nonextractable ^{14}C-activity in the 15 bar soils were smaller than those in soils maintained at lower soil-water tensions. No consistent trend was noted for the formation of nonextractable ^{14}C-activity in soils maintained at soil-water tensions of 0.1, 0.33, and 1 bar. Less ^{14}C-activity in soils incubated at 15°C became nonextractable than at 27° and 35°C, while % of nonextractable ^{14}C-activity in soils maintained at 35°C were smaller than in soils maintained at 27°C with the exception of the Houston soil. As much as 94.5% of applied ^{14}C-activity in the Houston soil at 35°C became nonextractable at the completion of incubation (28 days). Substantial amount of ^{14}C-activity in the ^{14}C-carbofuran treated soils incubated aerobically and anaerobically were reported by other investigators (Getzin, 1973; Venkateswarlu and Sethunathan, 1979). Getzin (1973) suggested carbofuran phenol was the hydrolysis product of carbofuran which formed the nonextractable ^{14}C in soils.

2,4-D

Mineralization rates--

The mineralization rate constants (k_1) and the half-lives ($t_{1/2}$) of uniformly ring-labeled ^{14}C-2,4-D in the Cecil and Webster soils are shown in Table IV-13. As indicated by the coefficients of determination (r^2), the mineralization rates approximated to first-order kinetics. The mineralization rates for soil maintained at soil-water tensions of 0.1 and 0.33 bar were not significantly different. Considerable amounts of ^{14}C-activity, ranging from 15.3 to 32.6% of applied-^{14}C remained in the soils at the completion of incubation (28 days). The percent of ^{14}C recoveries from $^{14}CO_2$ evolution plus ^{14}C-remaining in the soils were all nearly 100%.

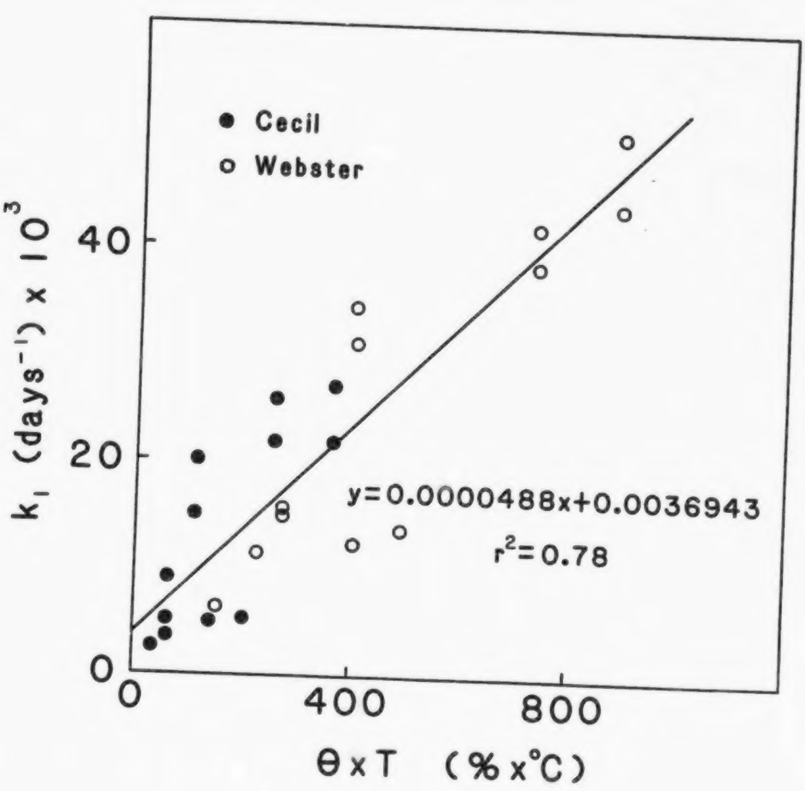

Figure IV-3. The relationship between the rate constants (k_1) solvent extractable ^{14}C-activity disappearance and soil-water content (θ) in Cecil and Webster soils and temperature (T).

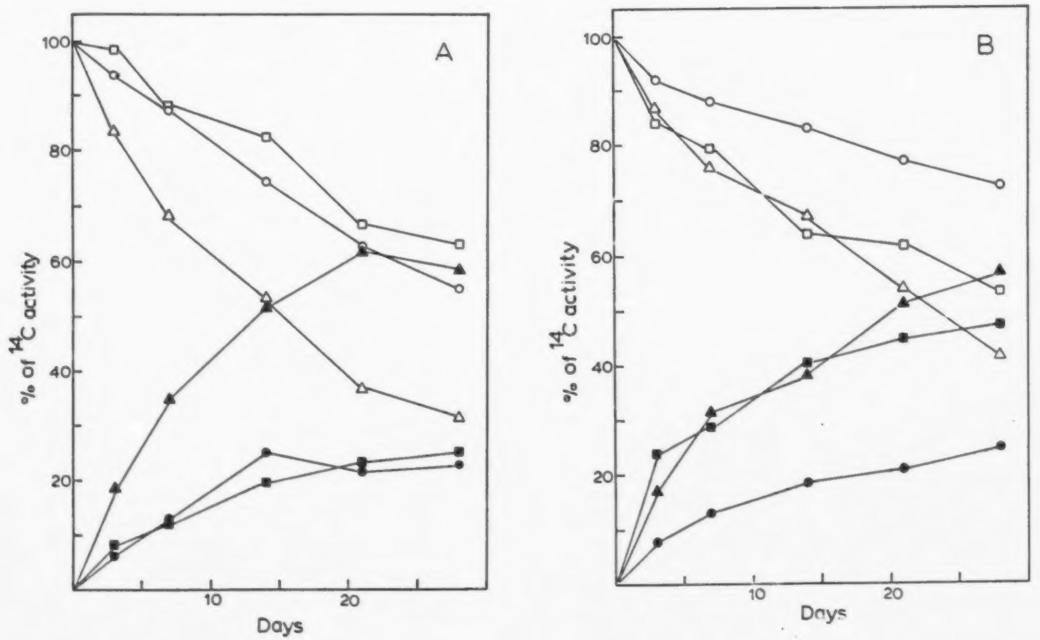

Figure IV-4. Extractable- and nonextractable-^{14}C-activity of ^{14}C-carbofuran treated soils maintained at 27°C and 0.33 bar of water tension during 28 days of incubation. Open symbols, extractable ^{14}C-activity; closed symbols, nonextractable ^{14}C-activity. A. ○ , Cecil; Δ, Webster; □ Grenada. B. ○ , Sharpsburg; Δ, Houston; □ , Yolo.

TABLE IV-12A. ^{14}C-Activity Distribution of ^{14}C-Carbofuran in Soils at the Completion of 28-Day Aerobic Incubation Period.

Water tension	Temperature	Extractable ^{14}C	Nonextractable ^{14}C	$^{14}CO_2$
bars	°C	%	%	%
		Cecil		
0.1	15	84.2	17.8	ND
0.1	27	54.2	23.1	6.8
0.1	35	48.3	17.4	ND
0.33	15	86.3	15.8	ND
0.33	27	55.2	22.9	5.9
0.33	35	50.2	13.7	ND
1	15	85.1	14.3	ND
1	27	64.4	21.2	ND
1	35	54.7	13.2	ND
15	15	92.2	7.1	ND
15	27	74.1	11.8	ND
15	35	93.2	5.1	ND
		Grenada		
0.1	27	63.9	24.4	5.7
0.1	35	48.2	11.2	ND
0.33	27	63.2	24.8	4.3
0.33	35	50.6	10.9	ND
1	27	62.1	25.9	ND
1	35	53.0	11.8	ND
15	27	64.2	25.8	ND
15	35	76.6	10.4	ND
		Houston		
0.1	27	32.6	65.1	4.8
0.1	35	2.8	94.5	ND
0.33	27	41.4	56.8	4.9
0.33	35	3.4	89.4	ND
1	27	41.0	57.2	ND
1	35	7.0	82.6	ND
15	27	78.6	38.4	ND
15	35	40.5	67.7	ND

TABLE IV-12B. ^{14}C-Activity Distribution of ^{14}C-Carbofuran in Soils at the Completion of 28-Day Aerobic Incubation Period.

Water tension	Temperature	Extractable ^{14}C	Nonextractable ^{14}C	$^{14}CO_2$
bars	°C	%	%	%
		Webster		
0.1	15	66.6	27.9	ND
0.1	27	24.6	63.1	7.9
0.1	35	32.8	52.9	ND
0.33	15	68.9	22.0	ND
0.33	27	31.4	58.6	7.1
0.33	35	36.4	50.1	ND
1	15	69.9	27.4	ND
1	27	40.6	56.5	ND
1	35	39.7	46.2	ND
15	15	80.9	23.1	ND
15	27	31.4	51.7	ND
15	35	70.0	40.4	ND
		Sharpsburg		
0.1	27	67.4	26.2	2.0
0.1	35	78.8	10.1	ND
0.33	27	72.4	24.7	1.9
0.33	35	82.0	10.4	ND
1	27	72.5	25.2	ND
1	35	82.7	10.3	ND
15	27	87.4	21.1	ND
15	35	88.3	8.8	ND
		Yolo		
0.1	27	47.9	49.4	6.3
0.1	35	ND	ND	ND
0.33	27	53.3	47.2	5.4
0.33	35	ND	ND	ND
1	27	65.4	41.9	ND
1	35	ND	ND	ND
15	27	80.4	30.1	ND
15	35	ND	ND	ND

TABLE IV-13. 2,4-D Mineralization Rate Constants in Soils.

Soil	Soil Water Tension (bars)	k_1 (days^{-1})	$t_{1/2}$ (days)	r^2	% $^{14}CO_2$ evolved	% ^{14}C remaining	% ^{14}C recovery
Cecil	0.1	1.06×10^{-1}	6.5	0.805	84.0	15.3	99.3
	0.33	7.88×10^{-2}	8.8	0.886	82.0	17.1	99.1
Webster	0.1	5.42×10^{-2}	12.8	0.830	70.5	30.4	100.9
	0.33	4.78×10^{-2}	14.5	0.863	68.5	32.6	101.1
Sharpsburg	0.1	7.28×10^{-2}	9.5	0.671	74.0	25.9	99.9
	0.33	6.83×10^{-2}	10.2	0.674	73.0	23.8	98.8
Grenada	0.1	5.33×10^{-2}	13.0	0.889	75.0	23.8	98.8
	0.33	5.75×10^{-2}	12.1	0.753	74.0	22.9	96.9
Yolo	0.1	>0.693	<1	-	82.6	14.9	97.5
	0.33	>0.693	<1	-	85.0	13.8	98.8

TABLE IV-14. 2,4-D Disappearance Rate Constants (k_1) and Half Lives ($t_{1/2}$) as well as Distribution of ^{14}C-activity Remaining in Soils After 28 Days of Incubation.

Soil-water tension, bars	k_1 days^{-1}	$t_{1/2}$ days	r^2	%Extractable ^{14}C	%Nonextractable ^{14}C	%Recovery ^{14}C
Cecil						
25°C						
0.1	1.78×10^{-1}	3.9	.96	0.7	14.6	15.3
0.33	1.77×10^{-1}	3.9	.99	0.8	16.9	17.7
1	1.67×10^{-1}	4.2	.97	0.9	19.7	20.6
15	7.40×10^{-2}	9.4	.72	8.7	4.7	13.4
35°C						
0.1	1.02×10^{-1}	6.8	.86	6.9	19.9	26.8
0.33	9.24×10^{-2}	7.5	.93	9.4	22.5	31.9
1	8.08×10^{-2}	8.6	.99	11.4	24.9	36.3
15	6.04×10^{-3}	114.7	.83	82.7	10.3	93.0
Webster						
25°C						
0.1	9.89×10^{-2}	7.0	.91	8.5	20.5	29.0
0.33	9.98×10^{-2}	7.0	.95	7.9	22.2	30.1
1	6.02×10^{-2}	11.5	.99	19.0	24.0	43.0
15	2.73×10^{-3}	253.9	.65	91.4	6.1	97.5
35°C						
0.1	1.04×10^{-1}	6.7	.92	6.3	21.2	27.5
0.33	3.46×10^{-2}	20.1	.94	37.2	20.5	57.7
1	2.54×10^{-2}	27.2	.99	50.0	18.2	68.2
15	3.93×10^{-2}	176.2	.94	89.7	6.9	96.6

Disappearance rates--

The disappearance rates of extractable ^{14}C-activity in soils incubated at 25°C and at 35°C (Table IV-14) were calculated based on the first-order kinetics. The rates approximated to first-order kinetics as indicated by r^2. The disappearance rates in soil incubated at 35°C were lower than the corresponding treatments maintained at 25°C with the exception of the 0.1 and 15 bar treatments of the Webster soil. The k_1 values for the 0.1 bar Webster soil maintained at 25°C and 35°C were not significantly different. The k_1 value for the 15 bar Webster soil maintained at 35°C was significantly higher than the same treatment held at 25°C. The temperature for maximal disappearance rate appeared to be between 25° and 35°C with the exception of the 15 bar Webster soil.

Metabolites--

The ^{14}C-activity in the solvent extracts was identified by thin layer chromatography-autoradiography to be mainly 2,4-D. Trace amounts of 2,4-dichlorophenol were detected in the first 14 days of incubation. In addition, 3 minor radioactive compounds were detected during the 28 days of incubation. The total ^{14}C activity of the metabolites summed never exceeded 5% of ^{14}C in the extracts. Therefore, it was reasonable to conclude that the disappearance rate of extractable ^{14}C represented the disappearance rate of extractable 2,4-D with less than 5% difference.

Bound residues--

The formation of nonextractable ^{14}C-activity in soils appeared to be directly related to the disappearance of extractable ^{14}C. As the extractable ^{14}C in the soils maintained at 1 bar and lower rapidly declined, the nonextractable ^{14}C was rapidly formed (Fig. IV-5 and -6). Extractable ^{14}C in the soils held at 15 bars disappeared slowly and the formation of nonextractable ^{14}C was slow. Even though extractable ^{14}C in the Cecil soil maintained at 15 bars and 25°C disappeared rapidly, rapid formation of nonextractable ^{14}C was not observed. By comparing the mineralization results of the soils maintained at 0.1 and 0.33 bar, the amount of applied ^{14}C not accounted for extractable- and nonextractable-^{14}C in the same treatments was about the same amount of applied ^{14}C mineralized to $^{14}CO_2$. This indicated that $^{14}CO_2$ evolution was the main pathway of applied ^{14}C loss in the soils.

Diuron

Mineralization rates--

The amounts of $^{14}CO_2$ evolved from the uniformly ring-labeled ^{14}C-diuron in six soils (Cecil, Webster, Grenada, Sharpsburg, Houston and Yolo) maintained at 0.1 and 0.33 bar of soil-water tension were no more than 2% of applied ^{14}C-activity during 60 days of aerobic incubation. It was estimated based on the first-order kinetics that the half-lives of diuron in soils were all larger than 1000 days. Substantial amounts of diuron degradation products were found to persist in soil and water (Bowmer and Adeney, 1978).

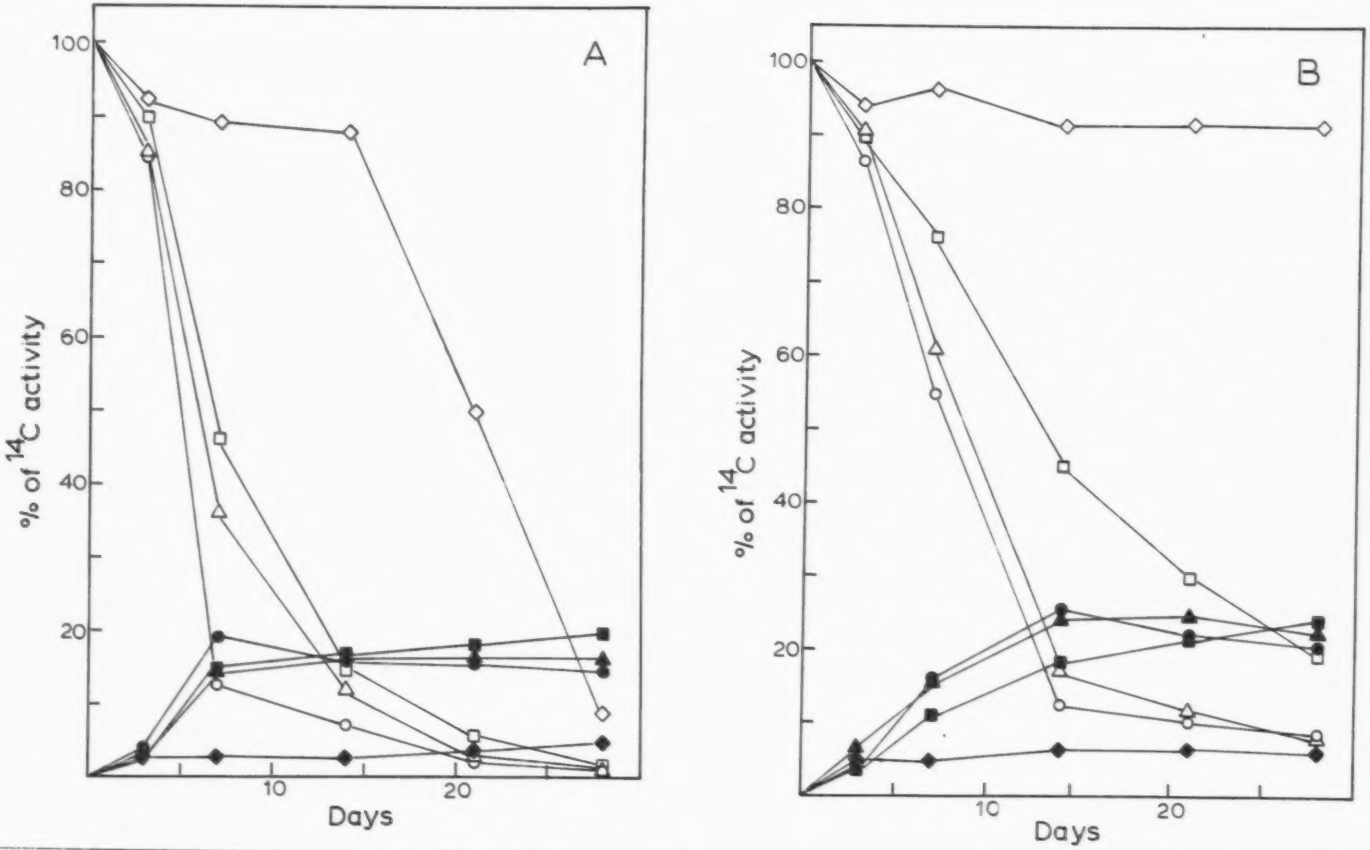

Figure IV-5. The distribution of extractable- and nonextractable-^{14}C-activity in the Cecil and Webster soils incubated at 25°C. Open symbols, extractable ^{14}C: ○, 0.1 bar; △, 0.33 bar; □, 1 bar; ◇, 15 bars. Closed symbols, nonextractable ^{14}C: ●, 0.1 bar; ▲, 0.33 bar; ■, 1 bar; ◆, 15 bars.

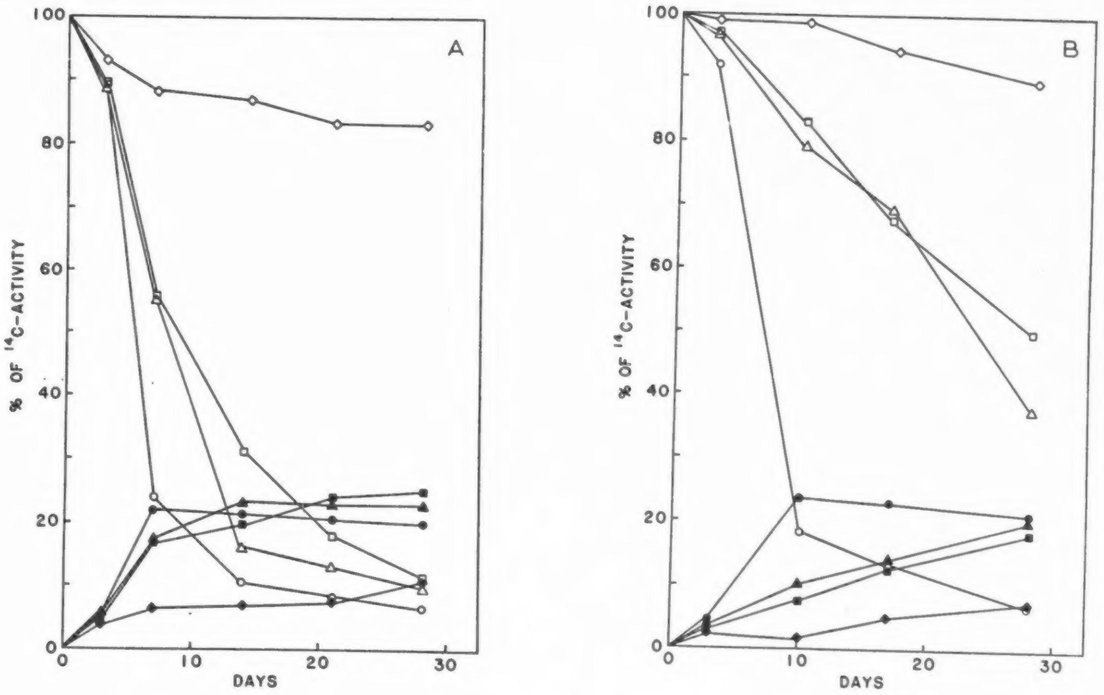

Figure IV-6. The distribution of extractable- and nonextractable-^{14}C-activity in the Cecil and Webster soils incubated at 35°C. Open symbols, extractable ^{14}C: ○, 0.1 bar; Δ, 0.33 bar; □, 1 bar; ◇, 15 bars. Closed symbols, nonextractable ^{14}C: ●, 0.1 bar; ▲, 0.33 bar; ■, 1 bar; ◆, 15 bars.

Fonofos

Mineralization rates--

Table IV-15 shows the mineralization rate constants (k_1) and the half-lives ($t_{\frac{1}{2}}$) of uniformly ring-labeled ^{14}C-fonofos in four soils (Cecil, Webster, Grenada and Sharpsburg) maintained at 0.1 and 0.33 bar of soil-water tension for 60 days. Determination coefficients (r^2) indicated that the degradation followed first-order kinetics. Mineralization was slow and the half-lives ranged from 260 to 1187 days with an average of 582 ± 320 days. Of applied ^{14}C-fonofos, 4-13% was evolved as $^{14}CO_2$ during 60 days of aerobic incubation.

Disappearance rates--

Similar to carbofuran and 2,4-D, the solvent-extractable ^{14}C-activity disappearance rates in soils were higher than the mineralization rates (Table IV-16). The disappearance rates in soils maintained at soil-water tension levels of 1 bar and below were generally not significantly different. The disappearance rates in the 15 bar soils were significantly lower than in the lower soil-water tension treatments. The Arrhenius activation energies (ΔE_a) in the Webster soil at temperatures 25°-35°C were small and were lower than those at temperatures 15°-25°C. The Arrhenius activation energies in the Cecil soils at temperatures 25°-35°C were higher than at temperatures 15°- 25°C. These findings suggested that microbial degradation was the main factor responsible for the degradation of fonofos in neutral soils such as the Webster soil, while chemical hydrolysis, in addition to microbial degradation, contributed to the fonofos degradation in acidic soils such as the Cecil soil.

Bound residues--

Table IV-17 shows the distribution of extractable- and nonextractable-^{14}C-activity in soils. The formation of nonextractable ^{14}C appeared to be directly related to the disappearance of extractable ^{14}C in soils. Extractable ^{14}C in the 15 bar soils disappeared more slowly than in the soils maintained at 1 bar and below. As a result the formation of nonextractable ^{14}C-residues in the 15 bar soils was lower. Increase in soil temperature enhanced the disappearance of extractable ^{14}C hence the formation of nonextractable ^{14}C increased. Lichtenstein, et al. (1977) reported that 46.8 and 35.3% of applied ^{14}C-fonofos were extractable and nonextractable, respectively, after 28 days of incubation in a moist silt loam soil.

TABLE IV-15. Mineralization Rate Constants (k_1) and Half-Lives ($t_{1/2}$) of Fonofos in Soils.

Soil-water tension, bars	k_1 days^{-1}	$t_{1/2}$ days	r^2
	Cecil		
0.1	9.01×10^{-4}	769	.982
0.33	8.26×10^{-4}	839	.991
	Webster		
0.1	2.66×10^{-3}	260	.963
0.33	1.80×10^{-3}	386	.969
	Grenada		
0.1	5.84×10^{-4}	1187	.815
0.33	1.38×10^{-3}	502	.959
	Sharpsburg		
0.1	2.11×10^{-3}	328	.953
0.33	1.80×10^{-3}	385	.951

TABLE IV-16. First-Order Rate Constants (k_1) and Half-Lives ($t_{1/2}$) for Disappearance of Extractable ^{14}C in Soils Treated with Fonofos.

Soil-water tension bars	Temp °C	k_1 $days^{-1}$ $\times 10^3$	$t_{1/2}$ days	r^2	k_1 $days^{-1}$ $\times 10^3$	$t_{1/2}$ days	r^2
			Cecil			Webster	
0.1	15	5.57	124	.925	11.90	58	.949
0.1	25	8.89	77	.860	21.50	32	.804
0.1	35	20.80	33	.972	23.30	30	.832
0.33	15	6.14	113	.983	12.90	54	.979
0.33	25	7.98	88	.805	21.20	33	.820
0.33	35	14.20	49	.958	25.10	28	.883
1	15	5.63	123	.980	11.30	61	.970
1	25	7.51	92	.796	19.90	35	.834
1	35	13.30	52	.934	21.70	32	.849
15	15	3.24	214	.991	8.11	86	.965
15	25	4.68	148	.803	17.40	40	.794
15	35	10.80	64	.926	19.80	35	.850
			Grenada			Sharpsburg	
0.1	25	16.30	43	.900	11.80	59	.945
0.33	25	17.90	39	.934	10.50	66	.943
1	25	14.40	48	.942	8.71	80	.845
15	25	11.30	61	.941	7.41	95	.940

TABLE IV-17. Distribution of Applied ^{14}C-Activity in Fonofos-Treated Soils at the Completion of 28-Day Incubation.

Soil-water tension bars	Temp °C	Extractable ^{14}C %	Nonextractable ^{14}C %	Extractable ^{14}C %	Nonextractable ^{14}C %
		Cecil		Webster	
0.1	15	84.3	8.4	70.2	28.3
0.1	25	76.0	17.4	45.7	46.9
0.1	35	54.8	19.9	44.6	43.2
0.33	15	84.0	10.4	68.5	30.1
0.33	25	76.9	15.7	47.0	45.1
0.33	35	65.9	19.0	43.4	43.6
1	15	84.6	7.4	71.9	27.4
1	25	78.9	11.3	49.5	42.6
1	35	67.3	24.6	48.8	40.4
15	15	91.5	5.2	79.0	17.3
15	25	85.4	9.3	52.8	40.3
15	35	73.2	14.3	52.3	37.7
		Grenada		Sharpsburg	
0.1	25	57.6	39.3	67.9	25.5
0.33	25	55.3	38.4	72.5	27.0
1	25	62.9	33.8	76.7	19.6
15	25	69.3	33.8	80.9	14.7

Methoxychlor

Mineralization rates--

Mineralization of uniformly ring-labeled ^{14}C-methoxychlor in four soils (Cecil, Webster, Grenada and Nebraska) was very slow. No more than 2% of applied ^{14}C-activity in soils maintained at 0.1 and 0.33 bar of soil-water tension was extensively degraded to $^{14}CO_2$ during a 60 day aerobic incubation period. It was calculated based on the first-order kinetics that the half-lives of ^{14}C-methoxychlor in the four soils were all over 1000 days ($k_1 < 6.93 \times 10^{-4}$ days^{-1}).

Methyl Parathion

Mineralization rates--

Methyl parathion was mineralized rapidly in both Cecil and Webster soils maintained at soil-water tension of 0.1 and 0.33 bar (Fig. IV-7); the difference between the two soil-water tensions was not significant. More than 40% of applied ^{14}C-methyl parathion was mineralized in 14d, and more methyl parathion was mineralized in the Webster soil than in the Cecil soil during the 28 day incubation period. Also, during this period about 0.1% of the applied ^{14}C was found in the ethylene glycol traps. This finding was confirmed that the amounts of ^{14}C remaining in soil and $^{14}CO_2$ evolved together were all nearly 100% (95-102%).

Disappearance rates--

Table IV-18 shows the solvent-extractable ^{14}C-activity disappearance rates of methyl parathion in the Cecil and Webster soils aerobically incubated at 25°C and maintained at soil-water tension levels of 0.1, 0.33, 1 and 15 bars. The rates approximated to first-order kinetics as indicated by determination coefficients (r^2). Extractable ^{14}C in soils maintained at 1 bar and below disappeared rapidly, and the disappearance rates were not significantly different, while the disappearance rates in the 15 bar soil treatments were significantly lower than the other three lower soil-water tension treatments.

Metabolites--

Table IV-19 shows the distribution of extractable ^{14}C-activity which was partitioned into water phase and hexane phase. The ^{14}C-activity in the H_2O extracts from the Cecil and Webster soils were about the same, except for the 15 bar treatments. The extractable ^{14}C-activity in the Cecil soil was higher than that in the Webster soil. Therefore, the ^{14}C-activity remaining in the hexane phase from the Cecil soil was higher. The distribution of extractable ^{14}C-activity in the water and hexane phase from the 15 bar Cecil soil was different from that in the Webster soil. The majority of extractable ^{14}C-activity in the Cecil soil was found in the hexane phase, while most of the extractable ^{14}C-activity in the Webster soil was found in the H_2O phase. TLC-autoradiographic analysis revealed that only the parent

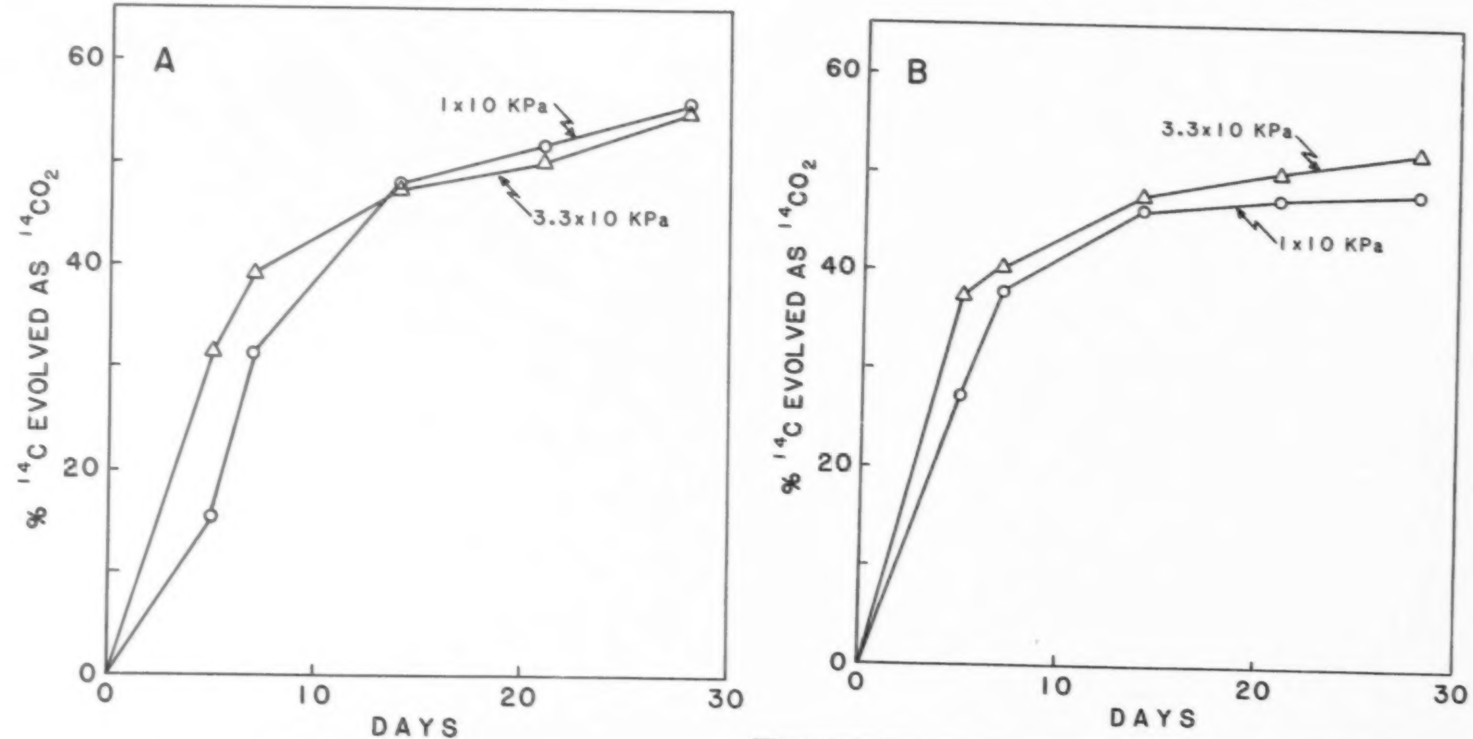

Figure IV-7. Mineralization of ^{14}C-methyl parathion in the Cecil (A) and Webster (B) soils maintained at 0.1 and 0.33 of soil-water tension.

TABLE IV-18. Rate of Solvent Extractable ^{14}C-activity Disappearance Rates in the ^{14}C-Methyl Parathion Treated Soils During 28 Days of Incubation.

Soil-water tension bars	k_1 $days^{-1}$	$t_{1/2}$ days	r^2	Extractable ^{14}C %	Nonextractable ^{14}C %	Recovery ^{14}C %
Cecil						
0.1	1.08×10^{-1}	6.4	0.97	5.4	31.5	36.9
0.33	1.04×10^{-1}	6.7	0.98	5.7	31.8	37.5
1	1.01×10^{-1}	6.8	0.99	6.0	33.6	39.6
15	2.96×10^{-2}	23.4	0.99	44.0	26.7	70.7
Webster						
0.1	3.02×10^{-1}	2.3	0.99	3.8	45.4	49.2
0.33	3.04×10^{-1}	2.3	0.99	3.6	39.4	43.0
1	2.92×10^{-1}	2.4	0.98	3.5	42.1	45.6
15	1.74×10^{-2}	39.8	0.89	55.2	35.7	90.9

TABLE IV-19. The Distribution of Extractable ^{14}C-Activity Partitioned into Water Phase and Hexane Phase.

Soil-water tension bars	^{14}C-activity* (%)			
	$\%^{14}C$ in water phase	$\%^{14}C$ in hexane phase	$\%^{14}C$ in water phase	$\%^{14}C$ in hexane phase
Cecil				
	7 days		14 days	
0.1	5.4	26.7	1.8	12.2
0.33	3.8	28.9	0.3	12.1
1	3.4	36.7	2.0	9.5
15	7.5	61.3	10.4	59.8
Webster				
0.1	3.2	7.5	1.6	4.2
0.33	3.0	8.7	1.2	4.3
1	4.1	9.0	1.4	4.1
15	57.8	20.0	48.0	9.5

*% of applied ^{14}C-activity

chemical methyl parathion was present in the hexane extracts, whereas p-nitrophenol and p-aminophenol were detected in the H_2O extracts. In addition to p-nitrophenol and p-aminophenol, trace amounts of 3 unidentified metabolites were detected in the H_2O extracts. The R_f values for methyl parathion, p-nitrophenol, and p-aminophenol were 0.55, 0.85, and 0.75, respectively. Because ^{14}C was labeled on the benzene ring, dimethylthiophosphate which could have been present in the H_2O extracts could not be spotted in the X-rays plates. Methyl aminoparathion was not detected in any of the treatments.

Soil-water tension appeared to have a great influence on the distribution of p-nitrophenol and p-aminophenol in soils. More p-aminophenol was detected in the 0.1 bar soils, while more p-nitrophenol was present in the 15 bar soils. As the soil-water tension increased from 0.1 to 15 bars the ratio of p-nitrophenol to p-aminophenol progressively increased (Table IV-20). Since methyl aminoparathion was not detected, it was unlikely that p-aminophenol was the hydrolysis product of methyl aminoparathion. Rather the metabolite was the product of p-nitrophenol reduction which was formed from the hydrolysis of methyl parathion. Adhya et al. (1981) reported that only trace amounts of methyl aminoparathion were accumulated in a flooded soil which had a redox potential of +100 mV. A decrease in soil-water tension would decrease oxygen tension in soil, hence soil redox potential was decreased. This would result in increase of anaerobic microbial activity which in turn would favor the reduction of p-nitrophenol to p-aminophenol.

Bound residues--

As the extractable ^{14}C-activity in the Cecil and Webster soils maintained at 0.1, 0.33 and 1 bar rapidly declined during the first 7d, the nonextractable ^{14}C-activity increased rapidly (Fig. IV-8). The formation of nonextractable ^{14}C-activity leveled off after 7 or 14 days. The formation of nonextractable ^{14}C-activity in the 15 bar soils was slow; however, it increased steadily during the entire 28d of incubation. Similar findings of rapid formation of nonextractable ^{14}C-activity as well as rapid disappearance of extractable ^{14}C-activity in moist silt loam soil (20% water content) treated with 1 μg/.g of ^{14}C-methyl parathion were also reported by Lichtenstein et al. (1977). The recoveries of extractable-plus nonextractable-^{14}C-activity in soils at the completion of incubation except for the 15 bar soils were very close, i.e. 36.9 to 39.6% for the Cecil soil and 43.0 to 49.2% for the Webster soil. The recoveries of extractable- plus nonextractable-^{14}C for the 15 bar soils were much higher amounting to 70.7 and 90.9% for the Cecil and Webster soils, respectively.

Propachlor

Mineralization rates--

Mineralization of uniformly ring-labeled ^{14}C-propachlor in five soils (Cecil, Webster, Grenada, Sharpsburg and Yolo) was slow and varied from soil to soil (Table IV-21). The rate constants (k_1) and half lives were

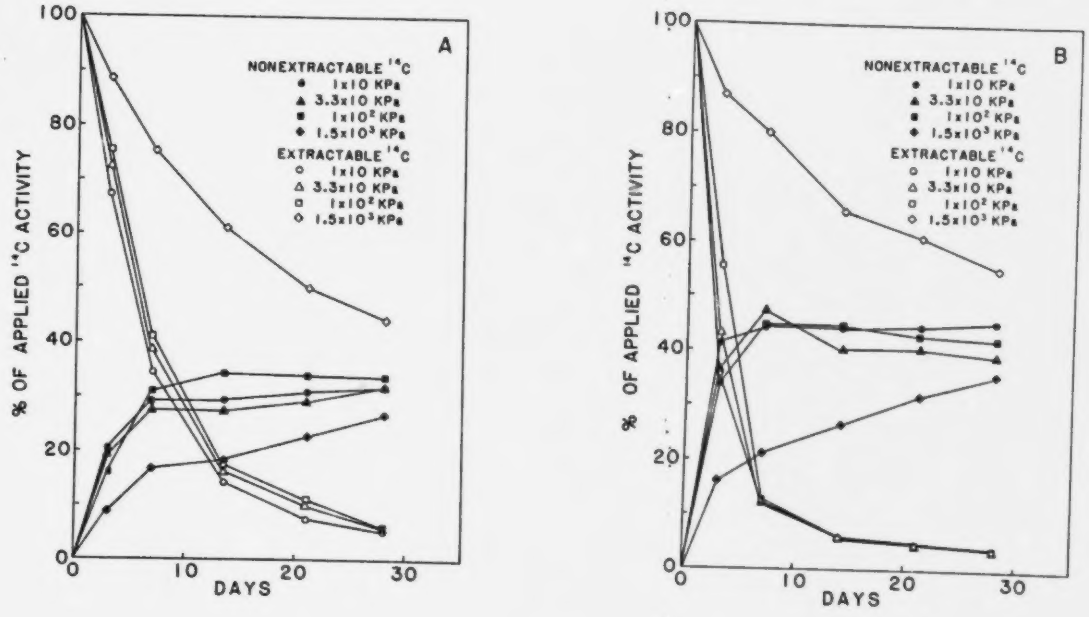

Figure IV-8. Distribution of extractable- and nonextractable-^{14}C in the ^{14}C-methyl parathion treated Cecil (A) and Webster (B) soils maintained at various soil-water tensions during a 28-day incubation period.

TABLE IV-20. The Influence of Soil-Water Tension on the Ratio of p-nitrophenol to p-aminophenol in Methyl Parathion-Treated Cecil and Webster Soils.

Soil-water tension bars	p-nitrophenol / p-aminophenol			
	7d	14d	7d	14d
	Cecil		Webster	
0.1	0.43	0.27	0.51	0.36
0.33	0.77	0.50	0.68	0.55
1	1.00	0.66	0.87	0.73
15	1.73	4.59	1.59	3.02

estimated by first-order kinetics and based on the results from 60 days of aerobic incubation. The half life in the 0.1 bar Webster soil was the shortest (379 days) and in the 0.33 bar Sharpsburg soil being the longest (1291 days). The average half life in the five soils was 923 ± 334 days. Mineralization in the 0.1 bar soils was significantly higher than in the 0.33 bar soils with the exception of the Yolo soil. However, the difference was small. After 60 days of incubation 3.0 and 10.5% of applied radioactivity in soils were mineralized to $^{14}CO_2$.

Disappearance rates--

The solvent extractable ^{14}C-activity disappearance rates in the Cecil and Webster soils were much higher than the mineralization rates (Table IV-22). The mineralization half lives for the Cecil and Webster soils were longer than 1000 and 350 days, respectively. The disappearance half lives for the Cecil and Webster soils were less than 21 and 18, respectively. Influence of soil-water tension on disappearance rates generally was insignificant except for the 15 bar soils incubated at 15°C. The half-lives in the 15 bar soils were significantly longer. The half-lives in the Cecil soil maintained at the four soil-water tension levels and 35°C were all shorter than 5 days.

Bound residues--

More than 50% of applied radioactivity in the Cecil and Webster soils became nonextractable after 28 days of aerobic incubation with the exception of the 15 bar soils incubated at 15°C (Table IV-23). The formation of nonextractable ^{14}C residues in the 15 bar soils incubated at 15°C was lower. This suggested that soil-water tension and soil temperature may have a concerted effect on the formation of nonextractable ^{14}C residues.

2,4,5-T

Mineralization rates--

2,4,5-T mineralization rate constants (k_1) and half lives ($t_{1/2}$) in four soils (Cecil, Webster, Sharpsburg and Yolo) maintained at 0.1 and 0.33 bar of soil-water tension and 25°C are shown in Table IV-24. 2,4,5-T in the 0.1 bar soils was mineralized significantly faster than in the 0.33 bar soils. At the end of 56 days of incubation period, 12.8 to 49.6% of applied ^{14}C-2,4,5-T was mineralized to $^{14}CO_2$. McCall et al. (1981) reported that 3 to 54% of applied ^{14}C-2,4,5-T in six soils was mineralized in 42 days of aerobic incubation and two metabolites 2,4,5-trichlorophenol and 2,4,5-trichloroanisole were detected.

TABLE IV-21. Mineralization Rate Constants (k_1) and Half Lives ($t_{1/2}$) of Propachlor in Soils.

Soil-water tension bars	k_1 days^{-1} x 10^4	$t_{1/2}$ days	r^2
		Cecil	
0.1	6.61	1049	.983
0.33	5.49	1263	.999
		Webster	
0.1	18.30	379	.997
0.33	14.80	470	.996
		Grenada	
0.1	7.17	967	.958
0.33	5.69	1219	.983
		Sharpsburg	
0.1	5.98	1160	.997
0.33	5.37	1291	.975
		Yolo	
0.1	9.13	759	.999
0.33	10.40	669	.999

TABLE IV-22. Rate Constants(k_1) and Half Lives ($t_{1/2}$) for Solvent Extractable ^{14}C-Activity Disappearance in Propachlor Treated Soils.

Soil-water tension bars	Temp °C	k_1 days^{-1} x 10^2	$t_{1/2}$ days	r^2	k_1 days^{-1} x 10^2	$t_{1/2}$ days	r^2
			Cecil			Webster	
0.1	15	3.28	21	.996	3.87	18	.996
0.1	25	4.70	15	.961	4.45	16	.932
0.1	35	>23.1	<3	-	4.48	16	.899
0.33	15	3.70	19	.981	4.32	16	.997
0.33	25	5.18	13	.967	4.69	15	.927
0.33	35	>23.1	<3	-	4.72	15	.920
1	15	3.63	19	.986	4.69	15	.998
1	25	5.38	13	.961	4.55	15	.887
1	35	>23.1	<3	-	4.34	16	.880
15	15	1.31	53	.976	1.52	46	.998
15	25	4.03	17	.988	4.63	15	.946
15	35	15.60	5	-	4.14	17	.953

TABLE IV-23. Distribution of Applied ^{14}C-activity in Propachlor-Treated Soils after 28 days of Incubation.

Soil-water tension bars	Temp °C	Extractable ^{14}C %	Nonextractable ^{14}C %	Extractable ^{14}C %	Nonextractable ^{14}C %
		Cecil		Webster	
0.1	15	40.5	58.2	33.6	64.0
0.1	25	26.5	69.9	26.8	70.6
0.1	35	24.8		24.2	73.5
0.33	15	36.5	58.9	31.2	63.2
0.33	25	23.3	75.0	24.7	73.7
0.33	35	24.2		22.8	74.6
1	15	37.1	56.5	27.2	67.6
1	25	21.8	72.3	27.1	70.4
1	35	22.6		24.5	72.1
15	15	70.2	22.9	65.6	32.5
15	25	29.9	62.8	30.8	67.3
15	35	23.9		29.0	69.3

TABLE IV-24. Mineralization Rate Constants (k_1) and Half Lives ($t_{1/2}$) of 2,4,5-T in four soils maintained at 0.1 and 0.33 bar of soil-water tension.

Soil-water tension bars	k_1 days^{-1}	$t_{½}$ days	r^2
		Cecil	
0.1	7.82×10^{-3}	88.6	.944
0.33	4.80×10^{-3}	144.4	.409
		Webster	
0.1	1.27×10^{-2}	54.7	.901
0.33	9.84×10^{-3}	70.4	.888
		Sharpsburg	
0.1	2.71×10^{-3}	256.1	.931
0.33	2.53×10^{-3}	274.3	.919
		Yolo	
0.1	1.47×10^{-2}	47.2	.948
0.33	9.00×10^{-3}	76.0	.960

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CHAPTER V

ESTIMATION OF ORTHOPHOSPHATE SORPTION ON SOILS

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INTRODUCTION

Modeling of phosphate loading rates in runoff waters requires a description of the phosphate retention processes in soils. Several processes may cause retention of phosphate by soil constituents and control the release of phosphate to runoff water. These processes include precipitation of solid phosphate-containing mineral phases, immobilization by soil biota, adsorption on solid surfaces, and ion exchange by positively charged soil colloids (Berkheiser et al., 1980).

Recent efforts to describe release phenomenon of phosphate to run-off waters have involved the use of empirical kinetic expressions (Sharpley et al., 1981a, b). Most nonpoint pollution models assume that the soil and solution are well mixed within the zone of interaction (Donigian et al., 1974; Davis and Donigian, 1979). Furthermore, reversibility of the phosphate sorption-desorption process is implicit in the model calculations, and parameters obtained from only phosphate sorption experiments are usually used to describe the partitioning of phosphate between soil or sediment and solution.

The mathematical description of phosphate sorption on a given soil has been relatively successful using the Langmuir, Freundlich, or Temkin adsorption equations. A "universal" quantitative description of the sorption process based on independent measurements of the number of phosphate sorption sites, however, has not met with a great deal of success. If a mathematical description satisfies the "universality" requirement, predictions of phosphate sorption by soils of varying composition could be made for a whole watershed. Provided with the required soil properties which are readily available in documents such as Soil Characterization reports of the State Agricultural Experiment Stations, the modeler could, presumably, predict phosphate concentrations in runoff waters without needing to measure sorption measurements on each soil at each location. If such data are not available or if verification is needed, soil properties could be more easily measured by standard laboratory procedures than phosphate sorption isotherms.

The objective of this work was to develop a "universal" mathematical description of phosphate sorption based on soil chemical and/or physical properties.

MODELS FOR SORPTION OF ORTHOPHOSPHATE

Three equations, developed for gas-solid systems, have been adapted for use in modeling the sorption of phosphate ions on charged surfaces. These are the Langmuir, Freundlich, and Temkin equations. Each equation can be developed from statistical mechanical considerations of gas adsorption by clean surfaces. The added restriction of electroneutrality $\Sigma z_i n_i = 0$, where n_i is the number of ions or ionized sites each with a charge of z_i, has made applications of these equations to electrolyte systems somewhat empirical. When applied to natural systems of a composite nature such as soils and sediments, these equations have been found to describe the adsorption of phosphate less than satisfactory over a wide range of phosphate concentrations (0-500 μg P/mℓ).

By far the most widely used model is the Langmuir equation which was originally applied to phosphate adsorption on soils by Olsen and Watanabe (1957). The simple Langmuir equation is written

$$\frac{C}{S} = \frac{1}{kS_{max}} + \frac{C}{S_{max}} \qquad [V\text{-}1]$$

where C = solution concentration of phosphate (μg P/mℓ), S = adsorbed phosphate at concentration C (μg P/g soil), S_{max} = adsorption maximum at which phosphate forms a monolayer on the solid surface (μg P/g soil), and k = a constant related to the bonding energy of the phosphate on the solid surface (mℓ/μg P). Validity of the parameters obtained from the Langmuir equation has been discussed recently (Holford, 1978; Harter and Baker, 1977, 1978; Veith and Sposito, 1977). The equation apparently has a statistical mechanical basis for ion exchange processes (Sposito, 1979).

Conceptually, Eq. [V-1] can be used to measure the amount of phosphate that a soil can adsorb. The equation has been utilized in describing the fertility status of soil phosphate (Fox and Kamprath, 1970; Olsen and Watanabe, 1957), since the parameter k is related to the bonding energy of phosphate to the soil and can be regarded as an "intensity" factor. Because k is related to the energy of adsorption, it may be useful in describing partitioning of phosphate between solid and solution phases. The S_{max} term has been related to "quantity" factors and as a measure of the capacity of a soil to retain phosphate. Both terms allow quantitative measures of phosphate availability to agricultural crops.

The quantitative measurement of phosphate partitioning between solution and solid phases remains largely undescribed. Causes of this deficiency rest largely in the lack of detailed knowledge of the structure and composition of the solid surface with which the phosphate reacts. Adsorption potential energies of surfaces in soil systems are not uniformly distributed. Each mineral and type of organic matter can be expected to adsorb phosphate with different adsorption energies. Surface areas contributing to each type of adsorbent are not likely to be equal.

Because of this nonuniformity of sorption site populations, Syers et al. (1973) used a curve-splitting technique, similar to the method developed by Shapiro and Fried (1959), to describe phosphate sorption by several Brazilian soils. The Langmuir equation, originally proposed to describe sites of more than one population (Langmuir, 1918), was written

$$S = \frac{k'S'_{max}C}{1 + k'C} + \frac{k''S''_{max}C}{1 + k''C} + \ldots . \qquad [V\text{-}2]$$

where the symbols are as defined for Eq. [V-1]; primes refer to site populations 1 and 2, respectively. In a similar manner, Holford et al. (1974) adapted the multi-site Langmuir equation to phosphate adsorption. Their equation was written the same as Eq. [2].

Holford et al. (1974) evaluated both the single-site and two-site equations and found correlation coefficients of 0.99 for the single-surface model (Eq. [V-1]) and 1.00 for the two-surface expression (Eq. [V-2]). Using regression coefficients for k and S_{max}, they found that Eq. [V-1] underestimates phosphate adsorption at low (0 to 2 μg P/mℓ) and high (>12 μg P/mℓ for slightly adsorbing soils) equilibrium phosphate concentrations. Both of these studies concluded that two populations of sites exist in soils for adsorption of phosphate. The strongly adsorbing population was characterized by high k values which were two orders of magnitude larger than those for the more weakly adsorbing populations.

Several empirical modifications of the Langmuir equations were introduced by Gunary (1970). Four equations were fitted to phosphate adsorption data of 14 soils by least-squares regression analysis and were written:

$$C/S = a + bC \qquad [V-3a]$$

$$C/S = a_1 + b_1C + d_1C^2 \qquad [V-3b]$$

$$C/S = a_2 + b_2C + d_2\sqrt{C} \qquad [V-3c]$$

$$\log C/S = a_3 + b_3\log C \qquad [V-3d]$$

Equation [V-3a] is seen to be in the form of the Langmuir equation and Eqs. [V-3b] and [V-3c] are modifications thereof. From their statistical analysis, they concluded that Eq. [V-3c] described the data better than the Langmuir equation. Eq. [V-3c] always gave S_{max} values that were 1.5 to 2.0 times that obtained from the Langmuir expression. Unfortunately, no theoretical foundation for Eqs. [V-3a] to [V-3d] was given and thus makes insight into the causes of phosphate adsorption difficult. However, including more arbitrary constants in the regression equation should improve the correlation.

The Freundlich adsorption equation was first applied to phosphate adsorption by Low and Black (1950). In their study of the correlation of phosphate adsorption with release of Al and Si from kaolinite, the equation used to adsorption of phosphate was

$$S = kC^{1/n} \qquad [V-4]$$

where S = phosphate adsorbed (μg P/g kaolinite), k = a constant (not necessarily equal to the Langmuir k), C = equilibrium concentration of phosphate (μg P/mℓ), and 1/n = constant. The authors reported values of k = 0.562 and 1/n = 0.388 for their kaolinite sample.

Fitter and Sutton (1975) used a modified Freundlich equation

$$S + a = bC^k \qquad [V-5]$$

where S = phosphate adsorbed in the experiment (μg P/g soil), a = constant which corrects for phosphate already present in the soil (μg P/g soil), C = equilibrium concentration of phosphate (μg P/mℓ), and b, K = constants. This equation appeared to describe phosphate sorption data on 29 soils from England. The value of a was determined by multiplying resin-extractable phosphate by a factor of 2.

Bache and Williams (1971) have used the Temkin equation for describing phosphorus adsorption by soils. The Temkin equation is stated as:

$$\frac{S}{S_{max}} = \frac{RT}{b} \ln(AC) \qquad [V-6]$$

where R = gas constant (cal mol^{-1} deg^{-1}), T = absolute temperature (°K), A, b are constants, and other symbols are as defined for Eq. [V-1]. The phosphorus adsorption isotherms plotted according to the Temkin equation were reported to deviate from linearity in a manner similar to that from Langmuir plots. Bache and Williams (1971) proposed a sorption index, dS/d ln C, obtained from the slopes of a plot of S versus ln C. Comparison of this sorption indices with other indexes gave significant correlations in most cases. For the soils tested by Bache and Williams, correlation coefficients of 0.99 and 0.28 were obtained, respectively, for regression of sorption index with the Langmuir constant S_{max} and k.

The above expressions are all derived for gas adsorption by solids and as such do not explicitly contain terms which consider ionic interactions. A model of ionic adsorption onto variable charge mineral surface was derived by Bowden et al. (1973a, b; 1977). Their derivation was based on the Stern model of the electrical double layer which is present at the interface between electrolyte solution and a solid surface composed of ionizable species. The model, unlike others, accounts for specific adsorption of ionic species from solution. This specific adsorption changes the potential Ψ_d (at the plane between the Stern layer and the diffuse layer) to a different extent than changes in Ψ_d imposed by changes in concentration of the indifferent electrolyte.

The model involves five equations in five unknowns. The applicable set of equations are written as Eqs. [V-7] to [V-11].

$$\sigma_i = \frac{N_i \Sigma z_i K_i C_i \exp(-z_i F\Psi /RT)}{1 + \Sigma K_i C_i \exp(-z_i F\Psi /RT)} \qquad [V-7]$$

$$\sigma_d = -1.22 \times 10^{-10} C^{\frac{1}{2}} \sinh(0.0195|z|\Psi_d) \qquad [V-8]$$

$$\sigma_s + \sigma_i + \sigma_d = 0 \qquad [V-9]$$

$$(\Psi_s - \Psi_d) = (4\pi d/\varepsilon_d)\sigma_s/G \qquad [V-10]$$

When hydrolyzable adsorbing species are considered, C_i can be expressed in terms of the total concentration of all forms of i in solution C_T, a_H, and the stepwise dissociation constants of all forms of i. For example, if $H_2PO_4^-$ is the adsorbing species, then

$$C_i = \frac{C_T K_1 a_H^2}{a_H^3 + K_1 a_H^2 + K_1 K_2 a_H + K_1 K_2 K_3} \qquad [V-11]$$

where K_1, K_2, and K_3 are stepwise dissociation constants of phosphoric acid.

The parameters N_s, K_H, K_{OH}, and G were estimated independently from titration curves of goethite in NaCl solution (a plot of log $_i$ versus pH at low surface coverage of i gives an intercept of log $(a_i)(K_i)$. ^{i}The parameters applicable to phosphate adsorption are described as follows: i = adsorbing species, e.g., H^+, OH_2^-, $H_2PO_4^-$, etc.; N_s = surface population density of adsorption sites (mol/cm^2); K_H, K_{OH} = binding constants of H^+ and OH^- ions on the metal oxide surface; K_i = binding constant of other adsorbing ions on the metal oxide surface, PO_4^{3-}, $H_2PO_4^-$; G = integral electrical capacitance of the region between the Stern layer (G can be computed using plots of the change in charge of the Stern layer with the change in pH); N = maximum number of ions adsorbed in the Stern layer; z_i = charge on ion i; C_i = concentration of adsorbing species i in the bulk solution; F, R = Faraday and gas constants, respectively; a_H = activity of hydrogen ions in bulk solution; σ_d = charge density at the interface between the Stern and diffuse layers; σ_s = charge density at the interface between the solid surface and the Stern layer; Ψ_d, Ψ_s = potentials at the respective interfaces; and ε_d = permittivity of the medium in the diffuse layer.

The above model has five unknowns, (σ_s, Ψ_s, σ_i, Ψ_d, and σ_d), independent variables (a_H, C_T, C_i), and the parameters (N_s, N_T, G, K_H, K_{OH}) can be estimated from acid-base titration curves of the the adsorbent in an indifferent electrolyte, while N_T and K_i can be determined from adsorption measurements (containing adsorbing species) at fixed ionic strength. The parameters thus measured can be substituted into Eqs. [V-7] to [V-11] which can then be solved.

After values for the parameters have been determined, the roles of the unknowns and independent variables can be assessed by interchanging the roles of the unknowns and the independent variable C_i. The Bowden et al. model predicted phosphate adsorption by goethite over a pH range of 2 to 11.

Other models for the adsorption of gases and vapors on solids have been introduced (Adamson, 1976). Each model attempts to describe the phenomenon of adsorption from basic physical and quantum parameters. Often the models apply to clean surfaces with uniform surface potentials quite unlike those found in soil systems. Recently, models have appeared which include surface heterogeneity in the treatment. In addition, a promising area of study would appear to be the inclusion of the additional condition of electroneutrality in the gas-solid adsorption models.

The models described above explain the experimental data satisfactorily in most cases for a given isotherm or solid phase. In nearly all cases, statistical fits of experimental data showed that the models predicted phosphate adsorption with correlation coefficients of 0.9 or higher. Because of assumptions made in model derivations, the goodness-of-fit does not necessarily correspond to correctness of the model when applied to other solids. Such solids may differ in bonding structure, porosity, crystallinity, and content of impurities. As a consequence of these variables, correlations of soil chemical and/or physical properties with sorption parameters obtained using the adsorption models would be empirical. The degree to which soil properties are correlated with sorption parameters has been tested and is the subject of the next section of this report. If the models are taken to describe phosphate adsorption adequately, the lack of correlation of model parameters with soil properties most likely results from inaccurate characterization of the adsorption mechanisms and poor description of sorption sites.

MATERIALS AND METHODS

Soil Collection

Six agricultural soils were collected from several states in order to represent a range of soil chemical properties. These will be referred to as EPA Project Soils. Eighteen soils were collected from the state of Florida based upon their diversity in mineralogy and clay content and will be referred to as Florida Soils. Twelve additional soils were received from Dr. Terry Logan (Ohio State University) for cooperation in a study of phosphate sorption protocols, and will be referred to as the Logan Soils. Geographical and classification data are summarized in Table V-1. All soils were air dried, passed through a 2 mm sieve, and stored for use.

Soil Chemical Characterization and Particle Size Analysis

Florida and EPA project soils were characterized with methods used by the Soil Conservation Service (1972). Exchangeable ions were extracted with pH 7.0, 1 $\underline{N}$ NH_4OAc and analyzed by atomic absorption spectroscopy (AAS). Values for pH were determined in H_2O, $\underline{1}$ KCl, and 0.01 $\underline{M}$ $CaCl_2$. Extractable Fe and Al were measured by the dithionite-citrate method, and the metals were determined by AAS.

Extractable acidity was determined by the $BaCl_2$-triethanolamine extraction. Pyrophosphate extractable Fe and Al were determined using $NA_4P_2O_7$ and analysis by AAS. Organic carbon was determined by acid dichromate digestion and titration to the diphenyl-aminesulfonate endpoint with ferrous ammonium sulfate. Conductivity was measured with a dip-type conductivity bridge on the saturation extract. Calcium carbonate equivalent was measured by addition of standardized HCl and back titration of excess acid with NaOH. Total phosphate was determined by Na_2CO_3 fusion of oven-dry soil and dissolution of the glass with $HClO_4$. Phosphate was determined spectrophotometrically by the ammonium molybdate method. Clay and silt contents were determined on soils which were previously treated with H_2O_2 to remove organic matter. Analyses of organic carbon and hense organic matter (above) and clay content (on soils dispersed in sodium hexametaphosphate solution and using the pipette method) were used to calculate silt content by difference. In every

Table V-1. Soil classification and geographical data.

Soil	Horizon	State	Classification	Textural class
Appalachee	Ap	FL	Fluvaquentic Dystrochrept	Sandy clay loam
Bethera	A1	FL	Typic Paleaquult	Loam
Bethera	B21tg	FL	Typic Paleaquult	Loam
Blount*	Ap	IN	Aeric Ochraqualf	
Cecil**	Ap	GA	Typic Paleudult	Loamy sand
Chalmers	Ap	IN	Typic Haplaquoll	
Clarion*	Ap	IA	Typic Hapludoll	
Conover*	Ap	MI	Udollic Ochraqualf	
Duplin	A1	FL	Aquic Paleudult	Fine sandy loam
Duplin	B2t	FL	Aquic Paleudult	Clay
Greenville	Ap	FL	Rhodic Paleudult	Fine sandy loam
Granada**	Ap	AR	Glossic Fragiudalf	Silt loam
Hornsville	A1	FL	Aquic Hapludult	Sandy clay
Hornsville	B21t	FL	Aquic Hapludult	Clay
Houston*	Ap	OK	Udic Paleustert	
Houston**	Ap	TX	Udic Paleustert	Clay loam
Hoytville*	Ap	OH	Typic Torrifluvent	
Lakeland (no P_2O_5)	Ap	FL	Typic Quartzipsamment	Fine sand
Lakeland (220 kg P_2O_5/ha)	Ap	FL	Typic Quartzipsamment	Fine sand
Locke*	Ap	MI	Aquollic Hapludalf	
Myakka*	Ap	FL	Aeric Haplaquod	Fine sand
Nicollet*	Ap	IA	Aquic Hapludoll	
Oktibbeha variant	A1+B21t	FL	Vertic Hapludalf	Sandy Clay
Orangeburg	Ap	FL	Typic Paleudult	Loamy sand
Orangeburg	B22tg	FL	Typic Paleudult	Sandy Clay
Orangeburg*	Ap	FL	Typic Paleudult	Loamy sand
Port*	Ap	OK	Cumulic Haplustoll	
Rossmoyne*	Ap	OH	Aquic Fragiudalf	
Sharpburg**	Ap	NB	Typic Argiudoll	Silty clay loam
Troup (high lime)	Ap	FL	Grossarenic Paleudult	Loamy sand
Troup (low lime)	Ap	FL	Grossarenic Paleudult	Loamy sand
Troup (virgin)	A1	FL	Grossarenic Paleudult	Loamy sand
Wauchula (lime)	Ap	FL	Ultic Haplaquod	Fine sand
Wauchula (virgin)	A1	FL	Ultic Haplaquod	Fine sand
Webster (virgin)**	Ap	IA	Typic Haplaquoll	Sandy clay loam
Yolo**	Ap	CA	Typic Xerorthent	Silt loam

*Soils used in conjunction with standard sorption method group (T. Logan).
**Soils used in conjunction with EPA.

case, a sample of soil from Florida was used to ensure quality control of analyses.

Soil Mineralogy

Mineralogy was determined by the usual x-ray diffractometric techniques modified from Jackson (1956). Carbonates and soluble salts were removed with NaOAc. The sample was placed into a 400 ml beaker. For each 10 gm portion of sample, 50 ml of 1 N sodium acetate (buffered to pH 5 with acetic acid) were added and the soil brought into suspension by stirring with a rubber policeman. The soil suspension was digested for 1 hour over a hot plate at low heat with intermittent stirring, after which the soil was transferred to a 250 ml polycarbonate centrifuge bottle for separation of the soil from solution phase. The supernatant was discarded.

For removal of organic matter, the sample in the centrifuge bottle was then wetted with NaOAc buffer and transferred to a 400 ml beaker with a minimum of water. Five ml of 30% H_2O_2 were added to each sample and stirred carefully. Addition of H_2O_2 was repeated twice with 10 ml of H_2O_2 and digested for two hours after each aliquot of H_2O_2 to insure completion of the reaction. The mixture was then reacted for two weeks at room temperature with daily additions of H_2O_2. To remove excess H_2O_2, the mixture was heated for 2 hours at 80-90°C. Reaction products from the soil were eliminated by addition of 100 ml of 1 N NaCl, mixing, and centrifugation. The solution was decanted and mineral matter recovered.

Free iron oxides were removed by treatment with sodium dithionite. Mineral matter was transferred to a 400 ml beaker (with 0.3 N Na-citrate), and 40 ml of 0.3 N Na-citrate and 5 ml of 1 N $NaHCO_3$ were added. The suspension was warmed carefully to 75-80°C in water bath and 1 gm of $Na_2S_2O_4$ was added with stirring. After digestion for 15 minutes, the suspension was cooled, centrifuged, and decanted. This treatment was repeated until the solution phase was not visibly colored with Fe (II). A sodium saturated sample was obtained by washing twice with 1 N NaCl.

The 2 μm clay fraction was obtained by centrifugation of the dispersed Na^+-saturated soil. An International No. 2 rotar was used with 250 ml centrifuge bottles and operated at 750 rpm for 5 min., 7 sec. After centrifugation, the <2 μm fraction was stored as a suspension.

For x-ray diffraction analysis, the aliquots of the suspension were removed for saturation with either Mg^{2+} or K^+. After washing the clays three times with 1 N chloride solutions and removal of excess salts, the Mg^{2+} clays were washed with 10% glycerol solution in order to obtain glycerol-solvated Mg^{2+}-saturated clays. The K^+-saturated samples were not treated with glycerol. Aliquots of salt-free suspensions were transferred to glass microscope slides and air-dried. X-ray diffractograms were recorded on a Diano XRD-700 X-ray Diffractometer at a scan rate of 2°2θ per minute using CuK_α radiation and a graphite monochromator. Mg^{2+}-saturated clays were analyzed air dry, and diffractograms of the K^+-saturated clays were recorded under air-dry conditions and after heating for two hours at 110°C and 300°C.

Evaluation of Methods for Determining Phosphate Sorption

The phosphate adsorption isotherms were obtained by equilibrating 1 g portions of air-dried soils with 25 ml of 0.01 M $CaCl_2$ solution containing 0, 0.2, 0.5, 1.0, 5.0, and 10.0 µg P as KH_2PO_4 per ml of solution in 50-ml capped polycarbonate centrifuge tubes. The equilibrium was assumed to be reached by shaking for 24 hrs in a rotating shaker at 19 ± 1°C. The contents were centrifuged and the supernatant solutions were analyzed for P by the ascorbic acid-reduced phosphomolybdate method (John, 1970). Solution pH at equilibrium was also determined. The amounts of P removed by the soils from the P solutions were considered being adsorbed by the soil and plotted against the equilibrium P concentration in the solutions according to Langmuir, Freundlich, and Temkin adsorption equations which are given as follows:

Langmuir I : $C/S = 1/kS_m + C/S_{max}$

Langmuir II : $S = S_m - S/kC$

Freundlich : $\ln S = \ln k + N \ln C$

Temkin : $S = S_{max}\,(RT/b) \ln AC$

$= S_{max}\,RT/b \ln A + S_{max}RT/b \ln C$

where S and S_{max} are the amount of P adsorption and adsorption maximum, respectively; C the equilibrium P concentration; k, N, A, and b are constants; R the gas constant and T the absolute temperature.

It was found that the P concentrations used in the adsorption studies were too low to obtain meaningful results for soils which have relatively higher P adsorption capacities. Therefore, the concentration range was later changed to 0, 1.0, 3.0, 5.0, 7.0, 10.0, 15.0, 20.0, 30.0, and 40.0 µg P/ml. Recent work showed that different electrolytes and their concentrations affect the P adsorption by the soils (Ryden and Syers, 1975; Ryden et al., 1977). Isotherms were also obtained for most of the soils studied in the presence of 0.03 M KCl which has the same ionic strength as 0.01 M $CaCl_2$. Under natural conditions, however, water is the liquid medium. Adsorption isotherms of 8 soils were obtained in water and in 0.03 M KCl and 0.01 M $CaCl_2$ for comparison. The protocol for determining phosphate sorption isotherms is being evaluated by a group of U.S. scientists under the direction of Dr. Terry Logan, and is as follows:

The proposed standard procedure for phosphate sorption isotherm for soils and sediments is as follows:

1. Weight of soil or sediment: 0.5 - 1.0 g.
2. Soil/solution ratio: 1/25.
3. Extraction time: 24 hours.
4. P concentration range: 0, 0.2, 0.5, 1.0, 5.0, 10.0 µg/ml as KH_2PO_4.
5. Electrolyte: 0.01 M $CaCl_2$, unbuffered.
6. Extraction system: 50 ml test-tubes, end-over-end shaker (maintain 50% air volume in tube for aeration).
7. Temperature: 25°±2°C.
8. Microbial retardation: 2% chloroform.
9. Duplication: duplicate extractions; single analysis of P in solution.
10. P analysis: any procedure with detection of 20-50 µgP.
11. Filtration: filter through 0.45 µ for soils coarser than clay loams and for finer soils if Technicon rapid P analysis method is used; centrifuge or filter through 0.2 µ for clay loam and clays soils and sediments.
12. Data representation: (a) P sorbed/desorbed versus equilibrium P concentration plot. Determine EPC_o and slope (buffer capacity at EPC_o).

Several parameters were selected from the isotherm plots according to the equations given previously. They included constant terms from various equations and the adsorption maxima from both Langmuir expressions. The adsorption maximum values as calculated from the quadratic equation (Yuan and Lucas, 1981) were also obtained. These parameters were related to selected soil properties.

Extractable Fe and Al

Experimental soils (Table V-1) were extracted by three different methods and analyzed for Fe and Al. All soils were air-dried and screened to pass a 2 mm stainless steel sieve. Aluminum and Fe were analyzed in the aqueous extract by atomic absorption using the nitrous oxide/acetylene and air/acetylene flame and the 309 and 248 mm wavelengths, respectively. The methods were as follows:

Method I - A 1.00 g soil sample was placed in 100 ml centrifuge tube and 40 ml of 0.3 M Na-citrate and 5 ml of 1.0 M Na HCO_3 were added. Tubes were placed in a water bath maintained at 80° ± 1°C and 1.0 g of solid $Na_2S_2O_4$ was added. Samples were stirred intermitently for 15 mins. A 10 ml aliquot of saturated NaCl solution was added and samples were mixed on a vortex mixer. Samples were centrifuged at 10,000 rpm and the supernatant placed in a 200 ml volumeric flask. The process was repeated with 0.5 g of solid $Na_2S_2O_4$ and the supernatant added to the 200 ml volumetric. All samples were brought to volume with Na-citrate and analyzed for Fe and Al (Mehra and Jackson, 1960).

Method II - A 1.0 g soil sample was placed in a 100 ml centrifuge tube and 40 ml of 0.2 M acidified ammonium oxalate (pH 3.3) was added. Tubes were stoppered and shaken in a light-tight reciprocating shaker box for 4 hrs. Samples were centrifuged at 10,000 rpm and filtered through Whatman NO. 40 filter paper and analyzed for Fe and Al (modified from McKeague and Day, 1966).

Method III- A 5.0 g sample of soil was placed in 30 ml centrifuge tubes and 25 ml of a 10^{-4} M CDTA solution was added. Tubes were shaken on a reciprocating box shaker for 4 hrs., centrifuged at 10,000 rpm filtered through No. 40 Whatman filter paper, and analyzed for Fe and Al.

Statistical Analysis

Data were analyzed using the Statistical Analysis System (SAS) provided as a computing package (Barr et al., 1976, 1979) by the North East Regional Data Center at the University of Florida.

SOIL CHARACTERISTICS

Soils representing seven soil orders were included in this study (Table V-1) and originated primarily from Ap horizons. A wide range in soil textures was apparent consisting of fine sands to clays. Various moisture regimes were also present and thus imposed different redox conditions on the soils.

The soil classifications can be considered in three groups because of the manner in which they were collected. Florida soils were composed of twelve Ultisols, two Entisols, two Spodosols, one Inceptisol, and one Alfisol. EPA Project soils include one Ultisol, one Alfisol, two Mollisols, one Vertisol, and one Entisol. Logan soils include four Alfisols, four Mollisols, one Vertisol, one Entisol, one Spodosol, and one Ultisol. Thus, the whole group of soils is composed of Ultisols (14), Mollisols (6), and Alfisols (6) and other orders (10).

Chemical characterization of EPA Project soils and Florida soils showed wide ranges in all properties measured (Table V-2). Water pH values ranged from 4.05 to 7.68; NH_4OAc extractable Ca ranged from 0.14 to 17.32 me/100 g. A wide range in citrate-dithionite extractable Fe and Al was also obtained (0.01 to 0.83% for Al and 0.27 to 4.20% for Fe). Additional data for all soils using several extraction methods will be presented in a later section.

Mineralogy of the soils (Table V-3) corresponded to the classification and chemical data. The Florida soils generally contained predominantly a combination of kaolinite-14°A Intergrade (or vermiculite)-gibbsite. They appeared to be typical of soils of the Southeastern United States. Several soils contained quartz, which commonly exists in the highly weathered soils of the region. Some smectite was observed in the Appalachee (a flood plain soil) and Hornsville Al (a soil from a depressional area). EPA Project soils contained a wide variety of minerals. Cecil soil from Georgia has mineralogy typical of the Southeast. Grenada from Arkansas contained less kaolinite and considerable mica. Houston, Sharpsburg, Webster, and Yolo contained higher percentages of smectite than the other soils. Mineralogy was not determined for the Logan soils. The presence of smectite generally corresponded to relatively high soil pH and exchangeable Ca. These four soils present a mineralogy quite different than the remainder of the soils because of the higher smectite content (expansible minerals) than the remaining soils which contain primarily non-expanding minerals typically found in a more severe weathering environment.

Vermiculite and 14°A Intergrade were distinguished on the basis of x-ray diffraction. The mineral was identified as vermiculite if the diffractograms showed collapse of the c-dimension to 10°A in a K^+-saturated specimen heated at 300°C for 2 hours. If the spacing remained at 14°A, the mineral was identified as 14°A Integrade. In some cases, interstratification of 10°A and 14°A clays was observed; these were identified as 14°A Intergrade, vermiculite or the reverse depending on which mineral predominated. Figures from Sawhney (1977) were used for this determination.

The wide variety of soil types, chemical and physical properties, and mineralogical compositions should provide a population of soils which will allow meaningful statistical comparison to be made for phosphate sorption studies. Based on recommendations in a review of phosphate sorption data (Berkheiser et al., 1980), the group of soils was collected and used for the collection of data for this project.

ADSORPTION ISOTHERMS

Evaluation of a Proposed Standard Procedure

Factors affecting the phosphorus retention by the soils have been discussed in a recent review (Berkheiser et al., 1980). Standardization of the procedure for soil P adsorption measurement seemed to be necessary from data presented. A group of soil scientists engaged in soil P research met in summer, 1979 at the annual meetings of the Soil Science Society of America and proposed a standard procedure for obtaining P adsorption

Table V-2. Chemical Properties of the Soils Used in the Study.

Soil Series	State	Horizon	pH			NH_4OA_c Extr. Bases, me/100g				Extr. Acidity me/100g	Cit.-dith. bicarb., %		Pyrophosphate extr., %		Organic Carbon, %C	Electrical Conductance, mmho/cm	Carbonate Content, %	Total P µg P/g soil
			H_2O (1:1)	1$\underline{N}$ KCl (1:1)	0.01$\underline{M}$ $CaCl_2$ (1:2)	Ca	Mg	Na	K		Al	Fe	Fe	Al				
Appalachee	FL	A	5.00	4.6	4.1	9.99	0.78	0.06	0.25	-	0.23	2.90	-	-	2.14	0.18	-	-
Bethera	FL	A1	4.7	4.3	4.0	2.75	0.26	0.01	0.13	-	0.02	0.27	-	-	2.33	0.25	-	-
Bethera	FL	B21tg	5.0	4.1	3.7	1.17	0.30	0.00	0.02	-	0.01	0.36	-	-	0.31	0.02	-	-
Cecil	GA	Ap	6.48	6.20	6.11	0.87	0.16	0.00	0.08	2.29	0.05	0.17	0.07	0.06	0.68	0.125	1.72	300
Duplin	FL	Ap	5.0	4.1	3.9	0.67	0.14	0.01	0.04	-	0.10	0.83	-	-	1.52	0.05	-	-
Duplin	FL	B21t	4.8	4.0	3.7	0.55	0.25	0.01	0.03	-	0.83	2.80	-	-	0.69	0.02	-	-
Grenada	AR	Ap	5.72	5.38	5.28	1.27	0.16	0.00	0.15	3.61	0.04	0.37	0.05	0.03	0.88	1.075	0.90	364
Greenville	FL	Ap	5.8	5.2	4.9	3.49	0.32	0.00	0.50	-	0.29	2.30	-	-	0.99	0.11	-	-
Hornsville	FL	A1	5.1	4.7	4.5	2.40	0.44	0.00	0.09	-	0.49	0.32	-	-	1.80	0.18	-	-
Hornsville	FL	B21t	5.0	4.2	3.8	1.90	0.63	0.01	0.03	-	0.39	2.40	-	-	0.29	0.02	-	-
Houston	TX	Ap	7.68	7.58	7.28	17.32	1.98	0.17	0.22	8.04	0.05	0.23	0.50	1.03	0.80	0.270	4.10	241
Lakeland (P)	FL	Ap	5.29	-	-	1.70	0.11	0.01	0.07	-	-	-	-	-	-	-	-	-
Lakeland (no P)	FL	Ap	5.33	-	-	1.63	0.11	0.02	0.07	-	-	-	-	-	-	-	-	-
Oktibbeha var.	FL	A1 B21t)	6.1	5.6	5.3	11.24	0.59	0.01	0.21	-	0.44	4.20	-	-	1.21	0.08	-	-
Orangeburg	FL	Ap	5.7	4.8	4.4	0.47	0.18	0.00	0.03	-	0.03	0.23	-	-	0.55	0.03	-	-
Orangeburg	FL	B22t	5.0	4.2	3.9	0.14	0.36	0.00	0.04	-	0.15	1.50	-	-	0.17	0.02	-	-
Sharpsburg	NB	Ap	5.56	5.48	5.33	6.07	2.22	0.00	0.34	10.92	0.08	0.56	4.26	7.38	1.80	0.540	2.65	599
Troup (high lime)	FL	Ap	5.21	-	-	2.50	0.41	0.03	0.12	-	-	-	-	-	-	-	-	-
Troup (low lime)	FL	Ap	5.93	-	-	1.43	0.29	0.05	0.08	-	-	-	-	-	-	-	-	-
Troup (virgin)	FL	Ap	6.28	-	-	2.13	0.17	0.02	0.06	-	-	-	-	-	-	-	-	-
Wauchula (limed)	FL	Ap	4.91	-	-	2.20	0.45	0.07	0.03	-	-	-	-	-	-	-	-	-
Wauchula (virgin)	FL	Ap	4.05	-	-	0.26	0.12	0.07	0.04	-	-	-	-	-	-	-	-	-
Webster	IA	Ap	7.37	7.15	7.01	13.65	1.81	0.00	0.20	6.11	0.05	0.42	0.17	0.24	3.34	0.285	2.90	675
Yolo	CA	Ap	6.92	6.62	6.58	4.80	4.94	0.04	0.56	5.64	0.04	0.50	0.04	0.02	1.35	0.335	6.87	804

Table V-3. Mineralogical Composition of <2 μm Fractions of The Soils Used.

Soils	Minerals present*
Appalachee	Kaolinite, smectite, vermiculite, mica
Bethera A1	Kaolinite, mica, vermiculite
Bethera B21tg	Kaolinite, vermiculite, smectite
Cecil Ap	Kaolinite, vermiculite, gibbsite
Duplin A1	Kaolinite, vermiculite, 14Å Intergrade, quartz
Duplin B2t	Kaolinite, vermiculite, gibbsite
Grenada Ap	Mica, vermiculite, kaolinite
Greenville Ap	Kaolinite, 14Å Intergrade
Hornsville A1	Kaolinite, vermiculite, smectite, mica, quartz
Hornsville B21t	Kaolinite, vermiculite
Houston Ap	Smectite, kaolinite, mica
Lakeland Ap (no P_2O_5)	14Å Intergrade, quartz
Lakeland Ap (P_2O_5)	14Å Intergrade, quartz
Oktibbeha A	Kaolinite, 14Å Intergrade, gibbsite, goethite
Orangeburg Ap	Kaolinite, 14Å Intergrade, vermiculite, gibbsite
Orangeburg B22tg	Kaolinite, gibbsite, vermiculite
Sharpsburg Ap	Smectite, kaolinite, mica
Troup Ap (virgin)	14Å Intergrade, gibbsite, kaolinite
Troup Ap (low lime)	14Å Intergrade, gibbsite
Troup Ap (high lime)	14Å Intergrade, gibbsite
Wauchula Ap (virgin)	Quartz
Wauchula Ap (limed)	Quartz
Webster Ap	Smectite, vermiculite, mica, kaolinite
Yolo Ap	Smectite, vermiculite, mica, kaolinite

*Listed in order of integrated intensities of the d(001) diffraction peak. The listing is not quantitative.

isotherm of soils and sediments. The procedure called for the shaking of 0.5-1.0 g portions of soil or sediment samples in an end-over-end shaker for 24 hours at 25 ± 2°C with 25 ml 0.01 M $CaCl_2$ in 50-ml tubes containing varied concentrations of P as KH_2PO_4. The initial concentration range proposed was from 0, 0.2, 0.5, 1.0, 5.0, to 10.0 μg P/ml. This procedure was evaluated.

Figure V-1 shows the data of five P adsorption isotherms obtained on different dates of Sharpsburg and Webster soils from Nebraska and Iowa, respectively. For better evaluation, the data were plotted according to the linear Langmuir equation (C/S vs. C). There were variations among the values at each P level from the five isotherms but very significant correlations were found for both soils between C/S and C when all the data points except the lower two P levels were subjected to the regression analysis. The correlations for the five individual isotherms were also highly significant. The data points from the lowest two P levels were erratic and far from the regression lines, and were not included in the adsorption isotherms. Therefore, the concentration of P for the studies under this project was changed to 0-40 μg/ml with the omission of 0.2 and 0.5 μg/ml. The extension to 40 μg/ml was to give more data points.

The effect of soil to solution ratio on P adsorption has been discussed elsewhere (Barrow and Shaw, 1979, Berkheiser et al., 1980). Barrow and Shaw (1979) investigated the conflicting reports on the effect of soil to solution ratio on P adsorption. They found no effect of soil to solution ratios on P adsorption if the shaking was gentle but vigorous shaking seemed to increase the rate of P adsorption of one soil at a narrow soil to solution ratio. The proposed standard procedure used in the present study included a ratio of 1:25 which was probably wide enough not to affect the P adsorption. A test was made to compare the P adsorption of Sharpsburg and Webster soils at this ratio with that at a 1:10 ratio, i.e. 5 g soil in 50 ml. In addition, isotherms were obtained form systems using the same 1:25 ratio as in the proposed standard procedure but both the amounts of soil and solution were doubled, i.e. 2 g soil in 50 ml solution. These adsorption isotherms are given in Fig. V-2. Only slight differences were noted. Therefore, the soil to solution ratio of 1:25 was adopted for the studies.

Effect of electrolytes used as the liquid medium in P adsorption studies has been observed by many workers. Ryden and Syers (1975) and Ryden et al. (1977) found that ionic strength and cationic species influenced P adsorption at the equilibrium concentration range of 0-10 μg/ml after 40 hours of contact. Singh and Tabatabai (1976) equilibrated soils with 0.01 M solutions of various metal chlorides containing 0-50 μg/ml by shaking for 24 hours and found that K, Na, Li, Ca, and Mg chlorides, Ca nitrate and sulfate, and K bicarbonate increased the soil P adsorption as compared to no-salt treatment. Rajan and Fox (1972) found that more P was adsorbed with $CaCl_2$ than with KCl and that increasing salt concentration increased the P adsorption. Since $CaCl_2$ at 0.01 M had been most widely used, it was decided that this electrolyte would be used as the main electrolyte in the present study. However, a test was made to measure the differences in magnitude of P adsorption between $CaCl_2$ and other commonly used electrolytes at the same

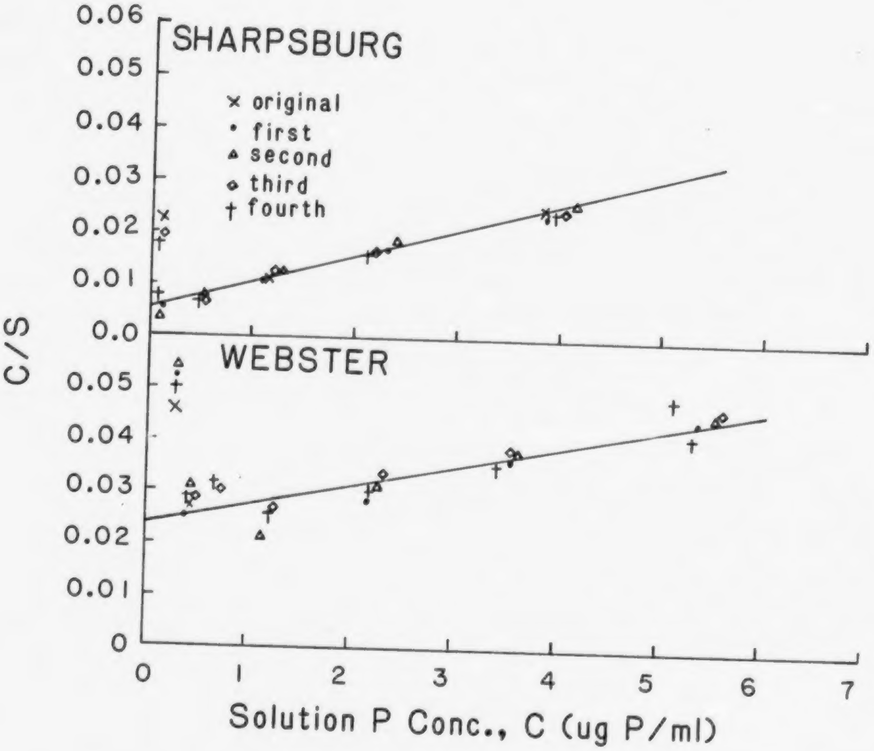

Figure V-1. Langmuir Plots for P Sorption on Sharpsburg and Webster Soils.

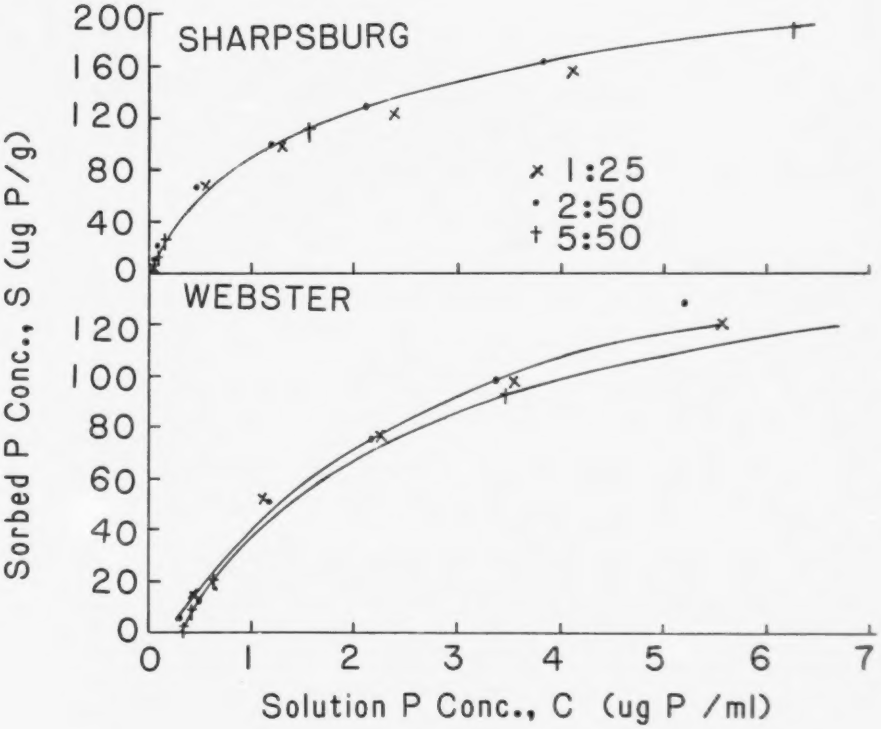

Figure V-2. P Sorption Isotherms Measured at Different Soil:Solution Ratios.

ionic strength. Results on Sharpsburg and Webster soils are shown in Fig. V-3.

As expected, the isotherms from the $CaCl_2$ system showed a greater P adsorption than from both KCl and NH_4Cl systems. The difference was smaller for the Sharpsburg than for the Webster soil. There were slight differences in P adsorption between 0.03 M NH_4Cl and 0.03 M KCl but the NH_4Cl system had a lower effect. The test was also done on several other soils. Similar results were obtained. The amount of P adsorption in the $CaCl_2$ system was invariably larger. It suggested that for practical application, the results from $CaCl_2$ tend to overestimate the P adsorption. Therefore, in addition to 0.01 M $CaCl_2$, KCl at the 0.03 M concentration was also used for the project soils as a comparison. It would be more realistic to use water as the liquid medium for P adsorption to simulate the natural soil condition. Because of the dispersion of fine soil particles as a result of prolonged shaking, a high-speed centrifuge would be needed to separate the supernatant solution from the colloidal material in the soil-H_2O suspension.

Linearization of Sorption Isotherms

Using the modified procedure (see above), a total of 65 adsorption isotherms were obtained. The data were plotted according to various adsorption models. These isotherms are presented in the Appendix.

The closeness of fit of adsorption data to different equations was examined by regression analysis. In addition to the original linear Langmuir equation and its modification, the Temkin and the linear Freundlich equations as well as the quadratic equation for P adsorption maximum calculation were also included. The correlation coefficients for the regression are shown in Table V-4. These coefficients were from both $CaCl_2$ and KCl systems in the P concentration range of 0-10 μg P/ml. Among the five models, Temkin, Freundlich, and Quadratic models were the best. The mean values of the regression coefficients for these three models were 0.90 ± 0.13, 0.94 ± 0.04, and 0.94 ± 0.05, respectively. Although the Langmuir equation has been used most widely for describing the P adsorption behavior of soils, the correlation was much lower than the other models (0.57 for the linear equation and 0.19 for its modification). The standard deviations of the regression coefficients were very high, 0.31 and 0.18, respectively.

To compare these models in more detail, the correlation coefficients were separated into two groups, based upon the electrolyte system, $CaCl_2$ and KCl, and two ranges of equilibrated P concentration, 0-10 and 0-40 μg P/ml. The mean correlation coefficients and their standard deviations are given in Table V-5.

The Temkin and Freundlich equations seemed to be comparable although the standard deviation was smaller with the Freundlich equation. The best fit was the quadratic equation. Not only it resulted in higher correlation coefficients but also the standard deviations were much smaller. In each case, the Langmuir and its modification did not give a correlation good enough to describe P sorption satisfactorily.

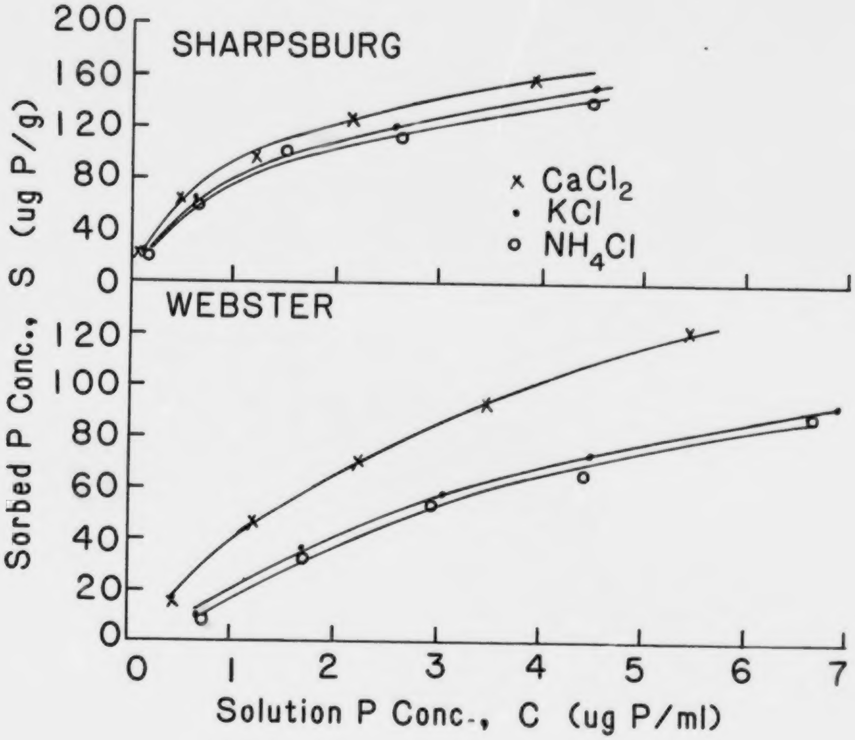

Figure V-3. P Sorption Isotherms Measured Using Three Electrolyte Solutions.

Table V-4. Correlation coefficients for regressions of each of five isotherm models to sorption isotherm data.

Soil	Electrolyte	R^{2*}				
		Lang. 1	Lang. 2	Freundlich	Temkin	Quad
Appalachee Ap	$CaCl_2$	0.03	0.15	0.94	0.48	0.92
Appalachee Ap	KCl	0.62	0.24	0.98	0.92	0.91
Bethera A1	$CaCl_2$	0.84	0.04	0.98	0.94	0.93
Bethera B21tg	$CaCl_2$	0.98	0.75	0.94	0.88	0.94
Bethera B21tg	KCl	0.99	0.74	0.98	0.98	0.93
Blount Ap**	$CaCl_2$	0.54	0.12	0.98	0.95	0.94
Blount Ap**	KCl	0.61	0.03	0.98	0.96	0.96
Cecil Ap***	$CaCl_2$	0.80	0.19	0.96	0.97	0.96
Cecil Ap***	$CaCl_2$	0.73	0.09	0.96	0.96	0.97
Cecil Ap***	KCl	0.45	0.12	0.78	0.85	0.98
Chalmers Ap**	$CaCl_2$	0.58	0.00	0.98	0.96	0.97
Chalmers Ap**	KCl	0.70	0.14	0.90	0.97	0.98
Clarion Ap**	$CaCl_2$	0.58	0.05	0.98	0.97	0.97
Clarion Ap**	KCl	0.56	0.18	0.98	0.98	0.99
Conover Ap**	$CaCl_2$	0.63	0.10	0.99	0.90	0.96
Conover Ap**	KCl	0.70	0.01	0.99	0.92	0.97
Dothan Ap	$CaCl_2$	0.06	0.22	0.42	0.98	0.82
Duplin A1	$CaCl_2$	0.91	0.53	0.96	0.85	0.96
Duplin B2t	$CaCl_2$	0.98	0.18	0.94	0.88	0.96
Duplin B2t	KCl	0.99	0.48	0.99	0.93	0.93
Greenville Ap	$CaCl_2$	0.16	0.18	0.97	0.92	0.88
Greenville Ap	KCl	0.74	0.08	0.96	0.97	0.91
Grenada Ap	$CaCl_2$	0.00	0.02	0.76	0.94	0.97
Grenada Ap	KCl	0.03	0.18	0.78	0.95	0.98
Hornsville A1	$CaCl_2$	0.00	0.23	0.74	0.96	0.92
Hornsville A1	KCl	0.44	0.01	0.56	0.78	0.80
Hornsville B21t	$CaCl_2$	0.99	0.65	0.8[illegible]	0.98	0.86
Houston Ap***	$CaCl_2$	0.44	0.02	0.95	0.96	0.97
Houston Ap***	KCl	0.39	0.00	0.94	0.97	0.99
Houston Ap**	$CaCl_2$	0.48	0.10	0.99	0.87	0.98

(continued)

Table V-4. Correlation coefficients of regressions of each of five isotherm models to sorption isotherm data (continued).

Soil	Electrolyte	R^{2*}				
		Lang. 1	Lang. 2	Freundlich	Temkin	Quad
Houston Ap**	KCl	0.49	0.03	0.99	0.91	0.98
Hoytville Ap**	$CaCl_2$	0.42	0.24	0.97	0.93	0.94
Hoytville Ap**	KCl	0.51	0.20	0.97	0.96	0.93
Lakeland Ap (no P)	$CaCl_2$	0.82	0.02	0.97	0.99	0.96
Lakeland Ap (p)	$CaCl_2$	0.82	0.08	0.76	0.92	0.82
Locke Ap**	$CaCl_2$	0.81	0.02	0.99	0.96	0.96
Locke Ap**	KCl	0.80	0.25	0.98	0.99	0.97
Myakka Ap	$CaCl_2$	0.73	0.04	0.94	0.91	0.93
Myakka Ap	KCl	0.33	0.08	0.99	0.93	0.99
Myakka Ap***	$CaCl_2$	0.87	0.27	0.99	0.98	0.94
Myakka Ap	KCl	0.64	0.42	0.96	0.93	0.97
Nicollet Ap**	$CaCl_2$	0.98	0.65	0.88	0.92	0.86
Nicollet Ap**	KCl	0.46	0.14	0.84	0.95	0.87
Oktibbeha Ap+B1	$CaCl_2$	0.12	0.23	0.87	0.96	0.90
Oktibbeha Ap+B1	KCl	0.50	0.19	0.98	0.92	0.90
Orangeburg Ap	KCl	0.99	0.81	0.99	0.97	0.94
Orangeburg Ap	$CaCl_2$	0.00	0.23	0.66	0.96	0.84
Orangeburg B22tg	$CaCl_2$	0.06	0.26	0.51	0.97	0.84
Orangeburg B22tg	KCl	0.11	0.08	0.75	0.95	0.88
Orangeburg Ap**	$CaCl_2$	0.74	0.18	0.97	0.92	0.85
Orangeburg Ap**	KCl	0.79	0.08	0.99	0.97	0.94
Porte Ap**	$CaCl_2$	0.72	0.01	0.98	0.96	0.96
Porte Ap**	KCl	0.67	0.04	0.98	0.98	0.98
Rossmoyne Ap**	$CaCl_2$	0.44	0.26	0.98	0.96	0.90
Rossmoyne Ap**	KCl	0.55	0.22	0.99	0.91	0.95
Sharpsburg Ap***	$CaCl_2$	0.10	0.22	0.83	0.97	0.97
Sharpsburg Ap***	KCl	0.36	0.13	0.93	0.97	0.98
Troup Ap (high lime)	$CaCl_2$	0.82	0.08	0.98	0.96	0.93
Troup Ap (low lime)	$CaCl_2$	0.82	0.04	0.98	0.95	0.91

(continued)

Table V-4. Correlation coefficients of regressions of each of five isotherm models to sorption isotherm data (continued).

		R^{2*}				
Soil	Electrolyte	Lang. 1	Lang. 2	Freundlich	Temkin	Quad
Troup Ap (virgin)	$CaCl_2$	0.93	0.16	0.99	0.98	0.87
Wauchula Ap (lime)	$CaCl_2$	0.93	0.26	0.93	0.94	0.96
Wauchula Ap (virgin)	$CaCl_2$	0.85	0.39	0.95	0.85	0.97
Webster Ap***	$CaCl_2$	0.16	0.25	0.95	0.98	0.99
Webster Ap***	KCl	0.00	0.48	0.85	0.99	0.99
Yolo Ap***	$CaCl_2$	0.86	0.12	0.87	0.86	0.98
Yolo Ap***	KCl	0.64	0.11	0.95	0.97	0.97

*Regression models used are as follows: Lang. 1: $C/S = 1/kS_{max} + C/S_{max}$; Lang. 2: $S = S_{max} - (1/k)S/C$; Temkin: $S = A + B\ln C$, A, B are constants; Freundlich: $\ln S = \ln K + N\ln C$; Quad: $S = a_0 + a_1C + a_2C^2$. In each case, the dependent variable (left-hand side of = sign) is a function of C or an arithemetic transformation of C.

**Logan Soils.

***EPA Project Soils.

Table V-5. Mean Correlation Values for Each of Five Adsorption Models With P Adsorption Data in $CaCl_2$ and KCl.

Electrolyte	Conc. range (μg P/ml)	No. of soils	Mean correlation coefficient*				
			Lang. 1	Lang. 2	Freundlich	Temkin	Quad
$CaCl_2$	0 - 10	37	0.59±0.34	0.20±0.18	0.94±0.04	0.90±0.13	0.93±0.05
	0 - 40	37	0.66±0.32	0.21±0.18	0.89±0.08	0.90±0.12	0.93±0.05
KCl	0 - 10	27	0.56±0.26	0.20±0.21	0.94±0.05	0.92±0.10	0.95±0.05
	0 - 40	27	0.67±0.26	0.18±0.13	0.90±0.06	0.94±0.07	0.95±0.05

*Correlation coefficient ± one standard deviation.

Sorption Parameter Estimation

As discussed in the preceding section, the Temkin, Freundlich, and quadratic models described well the soil P adsorption behavior. The first two were in linear forms. The constant terms from the two equations as well as the P adsorption maximum from the quadratic equation (Yuan and Lucas, 1981) were calculated for each soil in both $CaCl_2$ and KCl systems. Table V-6 lists symbols used to describe these constants in subsequent tables. Sorption parameters are given in Table V-7 and V-8 and were correlated with various soil properties. The constants from the two Langmuir equations were also tabulated for comparison.

Both linear Temkin and Freundlich equations contained logarithmic terms which are derived from the assumption that the energy of adsorption decreased exponentially with the surface coverage. The parameters for the Temkin model were the intercept constant A and slope B in the equation, $S = A + B \ln C$. Those for Freundlich were the intercept ln K, K, and the slope N in in the linear equation, $\ln S = \ln K + N \ln C$. The only parameter from the quadratic equation to be used for the correlation studies was the adsorption maximum. Since the constants from the Temkin and Freundlich equations have no specific physical meaning, the magnitude of these values in Tables V-7 and V-8 are difficult to interpret. The adsorption maxima obtained from the quadratic equation represent the P adsorption capacities of the soils. These values were less erratic than those from the two Langmuir expressions, although one value was negative, probably because one or two data points were out of place (Yuan and Lucas, 1982). Eight of the "high adsorption maximum soils", (>200 µg/g soil) belonged to the highly weathered Alfisols and Ultisols. The remaining three soils were a Mollisol, a Vertisol, and an Inceptisol. A comparison of results in Tables V-7 and V-8 also revealed that the adsorption maxima was higher in the $CaCl_2$ system than in KCl, indicating the electrolyte effect on P adsorption. It was in agreement with the results shown in Fig. V-2 that one tends to overestimate the amount of P adsorption if the measurement is made in a $CaCl_2$ system.

CORRELATION OF SORPTION PARAMETERS WITH SOIL PROPERTIES

Prediction of phosphate sorption by soils used in this study will be developed from correlation of phosphate sorption parameters with soil properties. Conditions under which data were collected for sorption parameters and soil properties include (a) only sorption of phosphate was measured at a single temperature; phosphate desorption was not studied; (b) soil chemical properties (extractable Fe, Al, and Ca) were obtained from extracts in which no attempt was made to exhaustively remove the total amount of element possible with a given reagent because only one extraction was made; (c) both 0.03 N KCl and 0.02 N $CaCl_2$ were used as electrolytes where 0.03 N KCl approximates natural conditions better than 0.02 N $CaCl_2$; and (d) observed sorption isotherms were linearized according to five models and calculated isotherms were based on the same models. Because conditions were more carefully controlled on a group of soils with a wide geographical distribution [compared to a collection of individual studies (Berkheiser et al., 1980), the variation in the magnitude of sorption parameters and soil chemical pro-

Table V-6. Definitions of Symbols Used in Regression Analyses.

Symbol	Definition of origin
PKL1	Langmuir k obtained from $C/S = 1/kS_{max} + C/S_{max}$.
PMAXL1	Langmuir S_{max} obtained from $C/S = 1/kS_{max} + C/S_{max}$.
PKL2	Langmuir k obtained from $S = S_{max} - (1/k)(S/C)$.
SMAXL2	Langmuir S_{max} obtained from $S = S_{max} - (1/k)(S/C)$.
KT	Intercept obtained from Temkin plot of S versus lnC in $S = (S_{max}\ RT\ln A)/b + (S_{max}\ RT/b)\ln C$.
SMAXT	Slope obtained from Temkin plot of S versus lnC in $S = (S_{max}\ RT\ln A)/b + (S_{max}\ RT/b)\ln C$.
NF	Freundlich exponent from $S = KC^{n}$.
NFI	Freundlich exponent from $S = KC^{1/n}$.
PKF	Freundlich K from $S = KC^{n}$.
FE1	Extractable Fe by Method II (dithionite), μmole/g soil.
AL1	Extractable Al by Method II, μmole/g soil.
FEAL1	Sum of FE1 and AL1.
FE2	Extractable Fe by Method I (oxalate), μmole/g soil.
AL2	Extractable Al by Method I, μmole/g soil.
FEAL2	Sum of FE2 and AL2.
FE3	Extractable Fe by Method III (CDTA), μmole/g soil.
AL3	Extractable Al by Method II, μmole/g soil.
FEAL3	Sum of FE3 and AL3.
CLAY	Percentage of clay in oven-dried soil.
SICL	Percentage of silt and clay in oven-dried soil.
CA	Ammonium acetate extractable Ca, μmole/g soil.
PH	Water pH (1:1/solution:soil) of soil.

Table V-7. Sorption Panameters for Soils in 0.1M KCL Electrolyte for Equilibrium Phosphate Concentrations of up to 10 µg P/ml.

Soil	PMAXL1	PKL1	SMAXL2	PKL2	KF	PKF	NF	NFI	KT	SMAXT	SMAXQUAD
	µg/g soil	ml/µg	µg/g soil	ml/µg	*	*	*	*	*	*	µg/g soil
Appalachee Ap	366.1	-2.438	237.7	29.58	5.59	268.64	0.389	2.570	295.0	55.87	453.7
Bethera B21tg	126.0	2.206	102.5	8.62	4.29	73.19	0.313	3.189	82.8	18.82	122.4
Blount Ap**	138.2	-2.130	92.6	4.52	4.09	60.08	0.528	1.893	80.1	33.71	169.2
Cecil Ap***	44.1	0.486	17.2	-2.03	2.32	10.26	0.856	1.167	20.3	10.93	50.0
Chalmers Ap**	77.5	-3.507	38.5	-1.68	3.53	34.44	0.612	1.633	43.3	26.28	98.1
Clarion Ap**	87.1	8.838	36.2	-1.24	3.35	28.78	0.731	1.367	39.7	28.24	96.5
Conover Ap**	120.3	-19.541	72.4	8.50	3.81	45.20	0.520	1.920	64.1	24.10	137.1
Duplin B2t	957.8	2.833	578.7	34.78	6.27	532.72	0.302	3.305	603.7	113.43	998.5
Greenville Ap	161.2	-2.403	112.8	4.91	4.41	82.68	0.448	2.229	105.3	32.21	193.8
Grenada Ap**	-23.7	-0.116	18.1	-0.97	1.85	6.36	1.334	0.749	20.7	17.17	61.0
Hornsville A1	103.2	4.331	63.4	-10.64	4.01	55.53	0.396	2.520	70.3	19.22	117.1
Houston Ap**	121.5	1.770	52.2	8.64	3.65	38.70	0.807	1.237	63.0	26.76	120.4
Houston Ap***	153.1	-1.413	110.0	4.07	4.29	73.33	0.577	1.731	102.7	36.79	204.8
Hoytville Ap**	215.6	-0.935	176.6	2.72	4.70	110.16	0.484	2.065	146.8	48.40	283.7
Locke Ap**	51.2	1.905	24.8	-1.49	2.84	17.11	0.575	1.737	21.2	13.81	52.1
Myakka Ap**	38.8	0.451	16.8	-1.28	1.98	7.27	0.745	1.341	9.7	9.98	33.3
Nicollet Ap**	228.3	-0.739	182.1	13.33	5.10	165.33	0.366	2.726	198.3	45.79	324.7
Oktibbeha A1+B21t	457.6	-1.235	289.9	2.59	5.70	300.06	0.287	3.474	337.0	66.45	616.5
Orangeburg B22tg	242.1	-1.071	244.2	24.85	6.04	422.25	0.529	1.887	410.4	100.39	544.5
Orangeburg Ap**	95.0	-2.730	80.1	6.25	4.04	56.93	0.377	2.647	65.1	22.55	111.5
Orangeburg Ap	113.1	1.824	94.0	5.18	4.13	62.24	0.331	3.015	70.6	18.16	112.4
Porte Ap**	81.8	-3.231	45.3	-3.43	3.61	37.22	0.576	1.735	48.5	23.61	97.7
Rossmoyne Ap**	210.0	-0.953	160.9	5.31	4.72	112.21	0.415	2.408	147.4	37.91	276.1
Sharpsburg Ap***	115.3	-2.007	84.6	3.61	4.22	68.64	0.688	1.452	93.1	29.28	152.4
Webster Ap***	-487.3	-0.266	22.0	-0.61	2.18	8.89	1.462	0.684	24.5	32.74	92.0
Yolo Ap***	89.6	13.658	54.3	3.06	3.57	35.54	0.638	1.567	53.3	18.84	97.9

*Because of the equations from which these parameters were derived, no units are given.

**Soils used in conjunciton with the standard sorption method group (Dr. T. Logan).

***EPA Project Soils.

Table V-8. Sorption Parameters for Soils in 0.02 N CaCl$_2$ Electrolyte for Equilibrium Phosphate Concentrations of up to 10 ug P/ml

Soil	PMAXL1	PKL1	SMAXL2	PKL2	KF	PKF	NF	NFI	KT	SMAXT	SMAXQUAD
	µg/g soil	ml/µg	µg/g soil	ml/µg	*	*	*	*	*	*	µg/g soil
Appalachee Ap	-12.3	-0.142	281.1	13.87	5.25	191.90	1.007	0.993	325.5	79.12	601.4
Bethera A1	118.7	23.675	75.0	8.47	4.04	57.32	0.381	2.621	71.4	19.51	131.0
Bethera B21tg	138.4	1.552	108.7	3.89	4.10	60.37	0.678	1.472	85.1	14.41	130.5
Blount Ap**	151.4	-1.110	120.8	4.06	4.48	88.57	0.480	2.080	113.7	33.95	207.2
Cecil Ap***	74.6	-3.912	43.8	5.20	3.55	34.88	0.549	1.818	49.6	14.50	87.3
Chalmers Ap**	142.0	-2.983	85.8	9.68	4.01	55.32	0.586	1.704	75.6	37.17	171.2
Clarion Ap**	89.4	-2.568	47.9	-2.92	3.72	41.40	0.634	1.576	55.0	28.60	111.9
Conover Ap**	138.3	-1.523	101.6	4.03	4.24	69.98	0.460	2.171	93.9	25.13	175.1
Duplin A1	292.2	0.514	209.3	1.88	4.71	111.60	0.339	2.948	118.3	50.42	-376.1
Duplin B2t	772.8	5.641	375.9	218.91	6.28	538.61	0.319	3.131	544.1	93.78	818.4
Greenville Ap	63.1	-0.318	132.4	-11.48	4.76	117.33	0.388	2.574	140.0	34.99	236.7
Grenada Ap***	9861.9	0.001	27.4	-4.62	2.77	16.10	0.928	1.076	33.9	16.58	78.4
Hornsville A1	16806.7	0.002	117.2	7.61	4.08	59.62	0.898	1.112	112.0	25.81	194.9
Hornsville B21t	803.9	3.740	559.0	18.59	6.16	475.80	0.374	2.667	534.6	97.79	851.3
Houston Ap**	118.8	5.729	60.1	4.93	3.85	47.32	0.766	1.303	71.4	26.47	127.6
Houston Ap***	215.1	-1.540	158.1	2.02	4.42	83.34	0.577	1.731	126.2	45.86	277.3
Hoytville Ap**	223.6	-0.776	198.5	3.75	4.94	141.03	0.474	2.105	181.9	48.08	326.4
Lakeland Ap (No P)	66.6	-3.744	40.7	-6.45	3.56	35.44	0.459	2.178	42.4	17.25	78.3
Lakeland Ap (P)	66.3	-4.374	37.3	-4.33	3.61	37.22	0.415	2.407	42.9	16.89	77.0
Locke Ap**	63.6	-5.995	37.8	-6.23	3.42	30.75	0.457	2.184	39.0	14.00	72.1
Myakka Ap**	38.0	1.871	20.1	-1.85	2.67	14.49	0.480	2.080	17.6	8.79	38.6
Nicolett Ap**	383.3	2.847	289.1	9.21	5.41	224.75	0.387	2.577	252.8	53.67	378.2
Oktibbeha A1+B21t	282.3	-0.333	315.4	1.58	5.76	317.38	0.413	2.419	373.1	88.32	663.6
Orangeburg Ap	-4051.9	-0.006	95.4	19.29	4.06	58.14	0.754	1.325	98.3	18.82	160.4
Orangeburg B22tg	425.0	-0.542	344.1	25.02	6.00	403.45	0.547	1.827	424.7	82.57	751.7
Orangeburg Ap**	122.4	-1.554	90.1	15.75	4.33	76.09	0.294	3.390	90.1	18.21	150.6
Porte Ap**	118.7	-7.237	72.6	8.52	3.83	46.38	0.514	1.942	62.9	26.10	136.3
Rossmoyne Ap**	221.7	-0.725	183.4	12.04	5.07	160.45	0.380	2.626	192.7	43.64	320.2
Sharpsburg Ap	367.2	0.225	96.4	3.44	4.34	76.78	0.874	1.143	101.4	29.66	158.7
Troup Ap (High L)	139.9	-5.371	94.0	6.23	4.29	73.11	0.415	2.405	92.0	23.85	163.5
Troup Ap (Low L)	115.2	-11.340	75.6	6.51	4.01	55.42	0.410	2.435	70.1	20.96	130.2
Troup A1	138.9	310.894	91.5	18.11	4.40	82.10	0.302	3.304	95.7	18.68	154.6
Wauchula Ap (Lime)	36.5	7.142	22.5	-2.49	2.89	18.15	0.402	2.482	22.5	7.15	40.6
Wauchula A1 (Virgin)	33.9	0.907	18.6	-2.14	2.29	9.91	0.604	1.655	16.7	5.45	31.8
Webster Ap***	42.8	-0.441	23.3	-0.90	3.30	27.30	0.988	1.011	47.9	34.75	117.3
Yolo Ap***	62.7	-3.725	49.4	5.41	3.62	37.33	0.526	1.898	50.9	15.33	100.5

*Because of the equations from which these parameters were derived, no units are given.

**Soils used in conjunciton with the standard sorption method group (Dr. T. Logan).

***EPA Project Soils.

perties probably represents true variability of the soil system. Other sources of variability are present whenever a collection is assembled from the literature.

The objective of this project was to develop a predictive equation which allows the calculation of partitioning between solid and solution phases of the soil-water system. In order to accomplish this objective, we proposed that phosphate sorption parameters could be estimated from soil chemical and/or physical properties (Berkheiser et al., 1980). From the data set developed during the past project year, predictive equations were developed. Three criteria were established during the initial data analysis stages in order to reduce the number of meaningless steps in the analysis procedure. These criteria were as follows:

1. Isotherm models must describe observed phosphate sorption on an individual soil with a correlation coefficient (R^2) of 0.5 or greater for solution concentrations up to 10 µg P/ml.

2. Estimators (based on soil properties) for constants in the isotherm models must describe both model constants with R^2 of 0.5 or greater.

3 Isotherm models (with constant estimated from soil properties) must predict phosphate sorption for an individual soil within a factor of two of the observed sorption.

Because the objective of this project was to describe a relationship between sorbed phosphate and that in solution, we chose to develop equations which would allow the user to calculate predicted phosphate sorption from one to three soil chemical or physical properties. Those properties were ones that were easily measured in the laboratory and in some cases were identical to properties published by soil characterization laboratories using Soil Conservation Service laboratory analytical methods. A summary of the symbols used for sorption parameters and soil properties was given in Table V-6.

Values for sorption parameters determined in KCl and $CaCl_2$ electrolytes were presented in Tables V-7 and V-8. Values for SMAXL2, PKF, SMAXT, and SMAXQUAD follow roughly the same trend for soils of equivalent sorption characteristics. SMAXL2 ranges from 18.6 µg/g soil to 559 µg/g soil in $CaCl_2$ electrolyte and from 16.8 µg/g soil to 578.7 µg/g soil in KCl electrolyte. Values for a given sorption parameter were generally higher in $CaCl_2$ electrolyte than in KCl electrolyte for a given soil. This phenomenon was discussed in a previous section of this report. Negative values of sorption parameters for some soils resulted from the linear regression analysis for all sorption isotherm data for a given isotherm regardless of the magnitudes of S and C. In all cases (except one for SMAXQUAD in $CaCl_2$, Table V-8), the negative values indicated poor fits to the data and were restricted to isotherms which were modelled by the two Langmuir equations. The low R^2 values of isotherm fits to linearized Langmuir equations provided further evidence that the Langmuir equations were not suitable as models which could be used to calculate sorption isotherms from soil properties.

Table V-2 summarizes the chemical and physical properties of the soils used for correlation with sorption parameters. Note that metals are given as moles/g soil and not as the usual g/g soil or meq/100 g soil. These units were used in order to conform to the assumption that, chemically, phosphate reacts with an individual metal ion. Thus, for a reaction with one mole of Fe, Al, or Ca, the masses of metals involved would be 56, 27, or 40 g, respectively. All data were punched onto computer cards and were verified with original laboratory calculations to assure accuracy of transposing processes.

Correlations of sorption parameters with soil properties was initiated by using a stepwise multiple linear regression model containing all the properties listed in Table V-7. The statistical procedure (Goodnight, in Barr et al., 1979) begins by finding the variable which produces the highest R^2. Another variable is added which yields the greatest improvement in R^2. Once the two-variable model is obtained, the procedure checks all other variables to determine if replacing either the first two variables with another would produce a higher R^2. The variables producing the highest R^2 are kept, and the procedure is repeated until no further significant improvement in R^2 is obtained. Results of this analysis are found in Tables V9a-d. This procedure provided statistics on which to select one or two properties which could be used as estimators for sorption parameters.

Selection of soil chemical properties was based on the magnitude of the R^2 value, and consistency within a given isotherm model. That is, we required that the soil properties selected must provide good estimates of both constants in a given isotherm model. From the lists in Tables V-10a through V-10d, and the presence of certain properties common to almost all regression equations, FE1, FE2, AL1, AL2, FEAL1, FEAL2, CA, and CLAY were selected for subsequent regression analyses. Tables V10a-d and Tables V-11a and V-11b summarize the regression equations and their R^2 values for KCl and $CaCl_2$ electrolytes for one- and two-property estimates of the sorption parameters. Table V10a-d contain regression estimates of sorption parameters obtained from Ap and B2 or only Ap horizons. Including parameters from B2 horizons improved R^2 for some parameters and properties and worsened the R^2 for other parameters and properties regardless of electrolyte. Because the number of B2 horizons included in the group of soils and the small differences in R^2 (generally ≤ 0.2) between correlations of parameters with the same variable, parameters and properties from B2 horizons were included in subsequent analyses.

The statistical analysis showed that using three soil properties to estimate model constants accounted for more of the variability (higher R^2) than using two soil properties and this in turn gave more satisfactory results than using a single property. However, the change in R^2 values in going from two to three property estimates was considerably less than the change in going from the one to the two property estimate. In many cases the R^2 differs by 0.01 to 0.04 units between the two- and three-property

Table V-9a. Best models found by the maximum R^2 improvement technique in regressions of phosphate sorption parameters on soil properties using data from only Ap horizons in KCl electrolyte.

Dependent variable	Regression equation	R^2
PMAXL1	= -47.60 + 997.7 AL2	0.44
	= -145.2 + 1029 AL2 + 1.79 SICL	0.49
	= -467.7 + 1196 AL2 + 74089 AL3 + 4.97 SICL	0.70
PKL1	= 2.73 - 12.64 AL2	0.18
	= 4.64 - 4471 FE3 - 11.18 AL2	0.27
	= 3.35 - 3841 FE3 + 13.52 AL3 - 11.4	0.32
SMAXL2	= 41.23 + 244.7 FE1	0.81
	= -4.68 + 1.96 CLAY + 298.4 FEAL2	0.85
	= -59.41 + 375.2 AL2 + 14886 AL3 + 3.62 CLAY	0.92
PKL2	= -1.72 + 107.1 FE2	0.64
	= 0.0264 + 188.6 FE2 - 31.18 FEAL2	0.75
	= 1.66 + 185.6 FE2 - 21.65 AL1 - 30.32 FEAL2	0.77
PKF	= 21.30 + 286.1 FE1	0.86
	= -32.68 + 2.44 CLAY + 334.8 FEAL2	0.88
	= -76.74 + 13381 AL3 + 3.68 CLAY + 311.4 FEAL2	0.92
NF	= 0.914 - 1.70 AL2	0.43
	= 1.12 - 1.856 AL2 - 103.8 AL3	0.68
	= 1.39 - 1.97 AL2 - 140.6 AL3 - 0.004 SICL	0.72
KT	= 36.01 + 304.65 FE1	0.85
	= -25.45 + 2.94 CLAY + 342.7 FEAL2	0.89
	= -67.54 + 12782 AL3 + 4.12 CLAY + 320.36 FEAL2	0.92
SMAXT	= 19.31 + 45.87 FE1	0.77
	= 6.50 + 57.65 AL2 + 0.718 CLAY	0.92
	= 9.66 + 48.52 AL2 + 0.917 CLAY - 0.112 SICL	0.93

Table V-9b. Best models found by the maximum R^2 improvement technique in regressions of phosphate sorption parameters on soil properties using data from only Ap horizons in $CaCl_2$ electrolyte.

Dependent variable	Regression equation	R^2
PMAXL1	= 4204 - 120.5 CLAY	0.09
	= 23358 - 4747259 FE3 - 3136 PH	0.18
	= 36765 - 8806 FE1 - 6599052 FE3 - 4846 PH	0.37
PKL1	= 50.1 - 46.46 AL1	0.20
	= 4.02 + 4.86 FE1 - 48.87 AL1	0.25
	= 6.90 + 28.70 FE1 - 120.7 FE2 - 69.4 AL1	0.54
SMAXL2	= 24.17 + 435.40 FEAL2	0.84
	= 3.39 + 1.48 CLAY + 397.17 FEAL2	0.87
	= -61.12 + 456.87 AL2 + 3.49 CLAY + 17543 FEAL3	0.94
PKL2	= 0.484 + 1663.5 FEAL3	0.16
	= 1.93 - 19.63 FE1 + 118.76 FE2	0.28
	= 0.0421 + 106.72 FE2 + 2147.5 AL3 - 26.10 FEAL2	0.36
PKF	= 12.64 + 488.90 AL2	0.70
	= -26.92 + 412.3 AL2 + 2.63 CLAY	0.87
	= -39.22 + 194.2 All + 420.5 AL2 + 2.47 CLAY	0.89
NF	= 0.515 + 0.00304 SICL	0.10
	= 0.710 + 3.04 FE2 - 0.674 FEAL1	0.26
	= 0.905 + 5.66 FE2 - 332.9 FE3 - 1.14 FEAL1	0.56
KT	= 20.76 + 475.55 FEAL2	0.80
	= -20.55 + 2.95 CLAY + 399.55 FEAL2	0.92
	= -31.86 + 177.23 AL1 + 2.78 CLAY + 406.87 FEAL2	0.93
SMAXT	= 13.62 + 99.54 FEAL2	0.69
	= 2.35 + 0.804 CLAY + 78.80 FEAL2	0.87
	= -3.03 + 7223 FE3 + 0.944 CLAY + 70.49 FEAL2	0.88

Table V-9c. Best models found by the maximum R^2 improvement technique in regressions of phosphate sorption parameters on soil properties using data from Ap and B2 horizons in KCl electrolyte.

Dependent variable	Regression equation	R^2
PMAXL1	= -26.06 + 661.63 FE1	0.57
	= -37.46 - 55.60 CA + 14.52 CLAY	0.66
	= -31.77 + 375.88 FE1 - 45.24 CA + 8.54 CLAY	0.74
PKL1	= 2.57 - 6.46 FEAL2	0.13
	= 4.27 - 3688.54 FE3 - 5.99 FEAL2	0.21
	= 4.07 - 3738.47 FE3 - 19.33 AL2 + 5.83 FEAL1	0.30
SMAXL2	= 29.99 + 369.03 FE1	0.72
	= -0.07 - 24.54 CA + 8.43 CLAY	0.84
	= 2.59 + 175.98 FE1 - 19.69 CA + 5.63 CLAY	0.91
PKL2	= -0.005 + 27.16 FE1	0.56
	= 3.47 + 82.90 FE1 - 54.77 FEAL1	0.64
	= 0.001 + 74.08 FE1 + 0.27 CLAY - 55.65 FEAL1	0.71
PKF	= -48.78 + 7.85 CLAY	0.67
	= -17.25 - 27.77 CA + 9.42 CLAY	0.86
	= -42.87 - 21.01 CA + 7.02 CLAY + 266.98 FEAL2	0.94
NF	= 0.87 - 1.51 AL2	0.40
	= 1.08 - 1.64 AL2 - 105.53 AL3	0.64
	= 1.25 - 1.66 AL2 - 127.20 AL3 - 0.002 SICL	0.66
KT	= -45.30 + 8.53 CLAY	0.71
	= -13.66 - 27.86 CA + 10.11 CLAY	0.88
	= -40.66 + 382.35 AL2 - 20.69 CA + 7.70 CLAY	0.95
SMAXT	= 2.28 + 1.56 CLAY	0.73
	= -1.62 + 1.12 CLAY + 58.08 FEAL2	0.86
	= 18.62 - 3.51 CA + 2.18 CLAY - 0.41 SICL	0.92

Table V-9d. Best models found by the maximum R^2 improvement technique in regressions of phosphate sorption parameters on soil properties using data from Ap and B2 horizons in $CaCl_2$ electrolyte.

Dependent variable	Regression equation	R^2
PMAXL1	= 3180 - 66.7 CLAY	0.06
	= 1326 - 7150870 FE3 + 2017095 FEAL3	0.14
	= 3221 - 8840645 FE3 - 20773 AL1 + 2277235 FEAL3	0.21
PKL1	= 4.42 - 36.02 AL1	0.14
	= 2.99 + 5.12 FE1 - 39.46 AL1	0.21
	= 5.19 + 12.28 FE1 - 47.49 AL1 - 15.35 FEAL2	0.35
SMAXL2	= 15.17 + 834.9 AL2	0.65
	= -32.92 + 563.9 AL2 + 4.017 CLAY	0.80
	= -2.50 + 437.5 AL2 - 15.44 CA + 5.1797 CLAY	0.85
PKL2	= -22.30 + 1.674 CLAY	0.32
	= -69.17 + 19942 AL3 + 2.284 CLAY	0.52
	= -50.66 + 15091 AL3 - 5.19 CA + 2.336 CLAY	0.57
PKF	= -44.80 + 8.11 CLAY	0.72
	= -6.13 - 28.26 CA + 9.202 CLAY	0.89
	= 67.1 - 24.4 CA + 10.92 CLAY - 2.210 SICL	0.95
NF	= 0.7575 - 0.6721 AL2	0.16
	= 0.6589 + 0.0370 CA - 0.2843 FEAL1	0.32
	= 1.275 + 0.0637 CA - 0.110 PH - 0.407 FEAL1	0.38
KT	= -23.48 + 8.566 CLAY	0.73
	= -68.20 + 609.4 AL2 + 5.75 CLAY	0.90
	= -35.89 + 475.1 AL2 - 16.41 CA + 7.000 CLAY	0.95
SMAXT	= 6.56 + 1.510 CLAY	0.73
	= -1.338 + 107.7 AL2 + 1.01 CLAY	0.90
	= -7.61 + 8371 FE3 + 97.7 AL2 + 1.14 CLAY	0.92

Table V-10a. Correlation of phosphate sorption parameters with single chemical or physical properties of soils. Phosphate sorption parameters were measured in KCl electrolyte and chemical and physical properties are from Ap and B2 horizons.

Dependent variable	Independent variable	Intercept estimate	Slope estimate	R^2
NF	FE1	0.7033	-0.498	0.22
	FE2	0.661	-0.988	0.08
	AL1	0.550	0.681	0.02
	AL2	0.731	-1.153	0.28
	FEAL1	0.710	-0.423	0.18
	FEAL2	0.738	-0.760	0.24
	CLAY	0.709	-0.004	0.04
PKF	FE1	14.33	390.0	0.64
	FE2	41.41	856.5	0.29
	AL1	89.92	254.5	0.01
	AL2	1.936	825.3	0.66
	FEAL1	1.408	357.9	0.60
	FEAL2	-8.948	573.4	0.65
	CLAY	-48.78	7.847	0.67
NFI	FE1	1.606	1.751	0.39
	FE2	1.886	1.690	0.03
	AL1	2.027	-0.304	0.0004
	AL2	1.540	3.790	0.43
	FEAL1	1.562	1.558	0.35
	FEAL2	1.578	2.189	0.29
	CLAY	1.819	0.012	0.05

(continued)

Table V-10a. Correlation of phosphate sorption parameters with single chemical or physical properties of soils. Phosphate sorption parameters were measured in KCl electrolyte and chemical and physical properties are from Ap and B2 horizons (continued).

Dependent variable	Independent variable	Intercept estimate	Slope estimate	R^2
KT	FE1	26.49	421.3	0.66
	FE2	63.61	818.5	0.23
	AL1	105.5	321.3	0.01
	AL2	16.11	867.4	0.65
	FEAL1	12.08	388.2	0.63
	FEAL2	7.870	586.4	0.60
	CLAY	-45.30	8.534	0.71
SMAXT	FE1	19.60	66.95	0.52
	FE2	22.69	168.3	0.31
	AL1	32.06	52.8	0.01
	AL2	17.42	142.1	0.54
	FEAL1	17.29	61.75	0.50
	FEAL2	14.73	102.8	0.58
	CLAY	2.282	1.563	0.73
PKL2	FE1	-1.224	33.71	0.70
	FE2	1.531	68.42	0.27
	AL1	5.493	18.79	0.008
	AL2	-1.293	63.27	0.57
	FEAL1	-2.309	30.83	0.66
	FEAL2	-2.235	44.50	0.58
	CLAY	-5.386	0.632	0.68
SMAXL2	FE1	31.10	366.5	0.68
	FE2	81.19	469.9	0.10
	AL1	99.09	292.9	0.02
	AL2	28.01	706.6	0.58
	FEAL1	18.43	338.2	0.64
	FEAL2	29.00	438.8	0.46
	CLAY	-27.94	7.041	0.66

Table V-10b. Correlation of phosphate sorption parameters with single chemical or physical properties of soils. Phosphate sorption parameters were measured in KCl electrolyte and chemical and physical properties are from Ap horizon only.

Dependent variable	Independent variable	Intercept estimate	Slope estimate	R^2
NF	FE1	0.711	-0.518	0.17
	FE2	0.764	-2.300	0.21
	AL1	0.583	0.550	0.01
	AL2	0.750	-1.309	0.27
	FEAL1	0.715	-0.410	0.13
	FEAL2	0.790	-1.042	0.31
	CLAY	0.718	-0.0025	0.01
PKF	FE1	21.05	283.2	0.73
	FE2	16.48	879.4	0.45
	AL1	56.79	279.4	0.04
	AL2	20.29	512.9	0.60
	FEAL1	11.85	252.3	0.69
	FEAL2	5.27	405.0	0.68
	CLAY	-10.27	4.657	0.46
NFI	FE1	1.607	1.63	0.28
	FE2	1.544	5.63	0.22
	AL1	1.894	0.224	0.0003
	AL2	1.476	4.175	0.47
	FEAL1	1.571	1.384	0.24
	FEAL2	1.390	3.083	0.46
	CLAY	1.800	0.00712	0.01

(continued)

Table V-10b. Correlation of phosphate sorption parameters with single chemical or physical properties of soils. Phosphate sorption parameters were measured in KCl electrolyte and chemical and physical properties are from Ap horizon only (continued).

Dependent variable	Independent variable	Intercept estimate	Slope estimate	R^2
KT	FE1	36.14	304.0	0.70
	FE2	31.18	945.0	0.45
	AL1	73.16	322.9	0.04
	AL2	35.80	546.1	0.56
	FEAL1	26.00	271.9	0.66
	FEAL2	19.61	432.4	0.64
	CLAY	-2.511	5.204	0.51
SMAXT	FE1	21.00	46.18	0.57
	FE2	19.63	153.1	0.40
	AL1	26.39	52.89	0.04
	AL2	21.66	76.07	0.38
	FEAL1	19.41	41.50	0.54
	FEAL2	18.90	63.24	0.48
	CLAY	10.18	0.950	0.68
PKL2	FE1	-1.201	30.62	0.64
	FE2	-1.881	97.98	0.42
	AL1	3.125	22.41	0.02
	AL2	-0.552	48.39	0.40
	FEAL1	-2.104	26.91	0.58
	FEAL2	-2.322	40.32	0.50
	CLAY	-5.420	0.575	0.52
SMAXL2	FE1	45.13	246.4	0.60
	FE2	38.84	801.0	0.40
	AL1	75.18	261.0	0.04
	AL2	43.86	452.2	0.51
	FEAL1	36.91	220.4	0.57
	FEAL2	30.01	360.7	0.59
	CLAY	15.29	3.931	0.43

Table V-10c. Correlation of phosphate sorption parameters with single chemical or physical properties of soils. Phosphate sorption parameters were measured in $CaCl_2$ electrolyte and chemical and physical properties are from Ap and B2 horizons.

Dependent variable	Independent variable	Intercept estimate	Slope estimate	R^2
NF	FE1	0.553	-0.0555	0.005
	FE2	0.522	0.332	0.02
	AL1	0.559	-0.350	0.01
	AL2	0.546	-0.0385	0.0006
	CA	0.493	0.00971	0.09
	FEAL1	0.557	-0.0592	0.01
	FEAL2	0.534	0.0435	0.001
	CLAY	0.545	0.0009	0.004
PKF	FE1	29.2	383.00	0.59
	FE2	68.7	712.00	0.18
	AL1	66.4	840.00	0.11
	AL2	16.9	819.00	0.61
	CA	62.8	1.02	0.01
	FEAL1	15.7	358.00	0.60
	FEAL2	16.8	542.00	0.54
	CLAY	-12.4	7.29	0.72
NFI	FE1	1.98	0.398	0.02
	FE2	2.14	-1.22	0.02
	AL1	2.00	1.17	0.01
	AL2	2.00	0.608	0.01
	CA	2.24	-0.0362	0.11
	FEAL1	1.96	0.382	0.03
	FEAL2	2.05	0.0709	0.0004
	CLAY	2.08	-0.0009	0.0004

(continued)

Table V-10c. Correlation of phosphate sorption parameters with single chemical or physical properties of soils. Phosphate sorption parameters were measured in $CaCl_2$ electrolyte and chemical and physical properties are from Ap and B2 horizons (continued).

Dependent variable	Independent variable	Intercept estimate	Slope estimate	R^2
KT	FE1	43.0	434.00	0.66
	FE2	84.9	859.00	0.22
	AL1	86.0	938.00	0.12
	AL2	29.9	923.00	0.67
	CA	132.	0.74	0.001
	FEAL1	27.9	406.00	0.67
	FEAL2	27.9	621.00	0.61
	CLAY	1.25	7.94	0.76
SMAXT	FE1	18.0	77.00	0.62
	FE2	23.8	179.00	0.29
	AL1	24.6	186.00	0.14
	AL2	15.4	166.00	0.65
	CA	29.6	0.96	0.05
	FEAL1	15.2	72.50	0.64
	FEAL2	14.2	116.00	0.64
	CLAY	7.84	1.48	0.78
PKL2	FE1	-5.64	78.22	0.30
	FE2	10.5	7.98	0.0002
	AL1	7.92	58.00	0.01
	AL2	-4.54	136.00	0.21
	CA	15.0	-0.820	0.02
	FEAL1	-7.42	69.40	0.28
	FEAL2	-0.966	69.10	0.11
	CLAY	-11.4	1.40	0.31
SMAXL2	FE1	56.0	352.00	0.56
	FE2	88.5	719.00	0.20
	AL1	88.2	809.00	0.11
	AL2	42.8	769.00	0.60
	CA	124.0	1.35	0.004
	FEAL1	43.3	330.00	0.57
	FEAL2	41.1	518.00	0.55
	CLAY	19.4	6.36	0.65

Table V-10d. Correlation of phosphate sorption parameters with single chemical or physical properties of soils. Phosphate sorption parameters were measured in $CaCl_2$ electrolyte and chemical and physical properties are from Ap horizon only.

Dependent variable	Independent variable	Intercept estimate	Slope estimate	R^2
NF	FE1	0.537	0.073	0.006
	FE2	0.518	0.588	0.02
	AL1	0.552	-0.0730	0.0003
	AL2	0.527	0.232	0.01
	FEAL1	0.536	0.058	0.004
	FEAL2	0.519	0.206	0.02
	CLAY	0.470	0.0077	0.17
PKF	FE1	41.5	225.00	0.50
	FE2	40.1	732.00	0.37
	AL1	55.6	441.00	0.11
	AL2	37.7	438.00	0.47
	FEAL1	33.3	210.00	0.52
	FEAL2	30.0	334.00	0.53
	CLAY	23.3	3.60	0.45
NFI	FE1	2.05	-0.0357	0.0001
	FE2	2.11	-1.38	0.01
	AL1	2.04	0.0006	0.0000
	AL2	2.06	-0.197	0.001
	FEAL1	2.05	-0.030	0.0001
	FEAL2	2.08	-0.303	0.005
	CLAY	2.34	-0.022	0.14

(continued)

Table V-10d. Correlation of phosphate sorption parameters with single chemical or physical properties of soils. Phosphate sorption parameters were measured in $CaCl_2$ electrolyte and chemical and physical properties are from Ap horizon only (continued).

Dependent variable	Independent variable	Intercept estimate	Slope estimate	R^2
KT	FE1	51.9	312.00	0.62
	FE2	47.7	1056.00	0.49
	AL1	76.3	516.00	0.09
	AL2	47.6	595.00	0.56
	FEAL1	41.5	286.00	0.62
	FEAL2	35.9	462.00	0.65
	CLAY	30.0	4.92	0.50
SMAXT	FE1	18.5	68.40	0.57
	FE2	16.9	245.00	0.51
	AL1	23.5	120.00	0.10
	AL2	17.7	129.00	0.51
	FEAL1	16.2	63.10	0.58
	FEAL2	14.8	102.00	0.62
	CLAY	10.2	1.26	0.60
PKL2	FE1	3.06	5.85	0.03
	FE2	2.17	35.40	0.07
	AL1	3.88	2.54	0.0003
	AL2	3.40	6.58	0.009
	FEAL1	2.93	5.03	0.02
	FEAL2	2.77	8.56	0.03
	CLAY	4.11	-0.002	0.000007
SMAXL2	FE1	61.0	262.00	0.46
	FE2	52.5	984.00	0.45
	AL1	84.5	376.00	0.05
	AL2	53.9	539.00	0.49
	FEAL1	52.9	238.00	0.45
	FEAL2	42.6	423.00	0.58
	CLAY	41.9	3.82	0.37

Table V-11a. Linear regression equations for estimating sorption parameters from two soil properties. Sorption property data were from Ap and B2 horizons in KCl electrolyte.

Dependent variable	Regression equation	R^2
SMAXL2	= 35.4 + 370 FE1 - 89.1 AL1	0.68
	= 30.4 + 366.7 FE1 + 0.110 CA	0.68
	= -16.8 + 240 FE1 + 3.59 CLAY	0.81
	= 105 + 290 AL1 - 0.887 CA	0.02
	= -18.5 - 153 AL1 + 7.09 CLAY	0.66
	= 83.8 + 467 FE2 - 0.368 CA	0.10
	= 28.7 + 41.1 FE2 + 6.95 CLAY	0.66
	= 19.1 + 716 AL2 + 1.21 CA	0.59
	= -50.3 + 454 AL2 + 4.66 CLAY	0.81
	= 32.0 - 118 FE2 + 744 AL2	0.59
	= 0.0737 - 12.3 CA + 8.43 CLAY	0.84
PKL2	= 0.427 + 34.4 FE1 - 16.7 AL1	0.71
	= -1.82 + 33.8 FE1 + 0.0882 CA	0.70
	= -4.38 + 21.7 FE1 + 0.321 CLAY	0.84
	= 5.53 + 18.8 AL1 - 0.00545 CA	0.01
	= -4.06 - 21.6 AL1 + 0.639 CLAY	0.69
	= 1.00 + 69.0 FE2 + 0.0761 CA	0.27
	= -6.08 + 38.6 FE2 + 0.543 CLAY	0.76
	= -2.66 + 64.7 AL2 + 0.186 CA	0.58
	= -7.07 + 34.2 AL2 + 0.453 CLAY	0.79
	= -2.13 + 24.7 FE2 + 55.4 AL2	0.60
	= -4.19 - 0.525 CA + 0.692 CLAY	0.72
KT	= 32.1 + 426 FE1 - 118 AL1	0.67
	= 27.9 + 421 FE1 - 0.215 CA	0.66
	= -34.5 + 233 FE1 + 5.18 CLAY	0.81
	= 114.5 + 317 AL1 - 1.36 CA	0.02
	= -33.5 - 192 AL1 + 8.59 CLAY	0.71
	= 66.5 + 815 FE2 - 0.419 CA	0.23
	= -52.5 + 401 FE2 + 7.60 CLAY	0.76
	= 7.17 + 876 AL2 + 1.22 CA	0.65
	= -72.2 + 545 AL2 + 5.67 CLAY	0.86
	= 10.1 + 178 FE2 + 810 AL2	0.66
	= -13.7 - 13.9 CA + 10.1 CLAY	0.88
SMAXT	= 20.4 + 67.6 FE1 - 17.0 AL1	0.52
	= 17.4 + 67.5 FE1 + 0.322 CA	0.53
	= 3.32 + 22.5 FE1 + 1.24 CLAY	0.76
	= 31.1 + 53.2 AL1 + 0.138 CA	0.01
	= 4.55 - 36.8 AL1 + 1.57 CLAY	0.73
	= 20.3 + 171 FE2 + 0.339 CA	0.32

(continued)

Table V-11a. Linear regression equations for estimating sorption parameters from two soil properties. Sorption property data were from Ap and B2 horizons in KCl electrolyte (continued).

Dependent variable	Regression equation	R^2
	= 0.613 + 93.1 FE2 + 1.35 CLAY	0.81
	= 13.2 + 146 AL2 + 0.569 CA	0.56
	= -1.68 + 80.3 AL2 + 1.14 CLAY	0.83
	= 14.9 + 75.0 FE2 + 118 AL2	0.59
	= 7.13 - 2.14 CA + 1.80 CLAY	0.85
KF	= 3.45 + 3.26 FE1 - 3.31 AL1	0.54
	= 3.15 + 3.16 FE1 + 0.0207 CA	0.53
	= 2.98 + 2.25 FE1 + 0.0222 CLAY	0.63
	= 3.94 + 0.0850 AL1 + 0.0116 CA	0.004
	= 3.19 - 5.03 AL1 + 0.0560 CLAY	0.53
	= 3.28 + 8.12 FE2 + 0.0220 CA	0.33
	= 2.79 + 5.15 FE2 + 0.0426 CLAY	0.61
	= 2.92 + 7.14 AL2 + 0.033 CA	0.62
	= 2.58 + 5.99 AL2 + 0.0231 CLAY	0.79
	= 3.05 + 3.36 FE2 + 5.82 AL2	0.62
	= 3.08 - 0.0900 CA + 0.0647 CLAY	0.59
NF	= 0.644 - 0.547 FE1 + 1.25 AL1	0.27
	= 0.669 - 0.490 FE1 + 0.00503 CA	0.24
	= 0.671 - 0.829 FE1 + 0.00771 CLAY	0.33
	= 0.506 + 0.702 AL1 + 0.00659 CA	0.04
	= 0.642 + 1.08 AL1 - 0.00452 CLAY	0.07
	= 0.624 - 0.948 FE2 + 0.00527 CA	0.10
	= 0.723 - 0.788 FE2 - 0.00237 CLAY	0.08
	= 0.709 - 1.13 AL2 + 0.00304 CA	0.28
	= 0.801 - 1.86 AL2 + 0.00558 CLAY	0.45
	= 0.735 - 0.104 FE2 - 1.12 AL2	0.28
	= 0.643 + 0.0292 CA - 0.00750 CLAY	0.21
NFI	= 1.71 + 1.84 FE1 - 2.20 AL1	0.42
	= 1.73 + 1.72 FE1 - 0.0179 CA	0.42
	= 1.94 + 2.62 FE1 - 0.0251 CLAY	0.50
	= 2.18 - 0.375 AL1 - 0.0229 CA	0.04
	= 1.97 - 2.51 AL1 + 0.0133 CLAY	0.08
	= 2.03 + 1.53 FE2 - 0.0210 CA	0.07
	= 1.80 + 0.742 FE2 + 0.0108 CLAY	0.06
	= 1.62 + 3.70 AL2 - 0.0117 CA	0.44
	= 1.58 + 4.90 AL2 - 0.0132 CLAY	0.50
	= 1.60 - 1.74 FE2 + 4.35 AL2	0.45
	= 1.98 - 0.0687 CA + 0.0203 CLAY	0.20

Table V-11b. Linear regression equations for estimating sorption parameters from two soil properties. Sorption property data were from Ap and B2 horizons in $CaCl_2$ electrolyte.

Dependent variable	Regression equation	R^2
SMAXL2	= 45.2 + 335 FE1 + 271 AL1	0.57
	= 50.6 + 351 FE1 + 1.11 CA	0.56
	= 20.0 + 188 FE1 + 3.87 CLAY	0.72
	= 83.3 + 803 AL1 + 1.05 CA	0.11
	= 18.2 + 31.7 AL1 + 6.32 CLAY	0.65
	= 84.4 + 715 FE2 + 0.868 CA	0.20
	= 14.8 + 307 FE2 + 5.75 CLAY	0.68
	= 31.3 + 775 AL2 + 2.21 CA	0.61
	= 0.0877 + 512 AL2 + 3.53 CLAY	0.80
	= 40.4 + 109 FE2 + 734 AL2	0.60
	= 34.1 - 11.6 CA + 7.69 CLAY	0.78
PKL2	= 2.67 + 82.7 FE1 - 74.7 AL1	0.31
	= -1.42 + 78.6 FE1 - 0.873 CA	0.32
	= -11.3 + 41.6 FE1 + 0.846 CLAY	0.34
	= 11.8 + 62.6 AL1 - 0.843 CA	0.02
	= -6.72 - 130 AL1 + 1.55 CLAY	0.33
	= 14.3 + 11.5 FE2 + 0.828 CA	0.02
	= -9.68 - 116 FE2 + 1.63 CLAY	0.35
	= -1.05 + 134 AL2 - 0.670 CA	0.22
	= -12.7 + 35.2 AL2 + 1.20 CLAY	0.31
	= -1.34 - 142 FE2 + 181 AL2	0.27
	= -6.01 - 4.27 CA + 1.88 CLAY	0.48
KT	= 32.4 + 418 FE1 + 267 AL1	0.67
	= 40.9 + 434 FE1 + 0.444 CA	0.66
	= 1.93 + 214 FE1 + 5.10 CLAY	0.83
	= 84.2 + 936 AL1 + 0.387 CA	0.12
	= 2.88 - 45.1 AL1 + 8.00 CLAY	0.76
	= 84.1 + 858 FE2 + 0.163 CA	0.22
	= -4.09 + 356.6 FE2 + 7.24 CLAY	0.79
	= 20.6 + 927 AL2 + 1.77 CA	0.68
	= -18.9 + 535 AL2 + 4.98 CLAY	0.88
	= 27.1 + 126 FE2 + 883 AL2	0.68
	= 17.6 - 12.9 CA + 9.42 CLAY	0.88
SMAXT	= 15.3 + 72.8 FE1 + 68.9 AL1	0.64
	= 13.6 + 76.6 FE1 + 0.914 CA	0.67
	= 7.94 + 33.6 FE1 + 1.03 CLAY	0.84
	= 20.4 + 181 AL1 + 0.898 CA	0.18
	= 7.22 + 16.9 AL1 + 1.46 CLAY	0.78
	= 19.9 + 175 FE2 + 0.848 CA	0.33

(continued)

Table V-11b. Linear regression equations for estimating sorption parameters from two soil properties. Sorption property data were from Ap and B2 horizons in $CaCl_2$ electrolyte (continued).

Dependent variable	Regression equation	R^2
	= 6.52 + 87.9 FE2 + 1.31 CLAY	0.84
	= 9.36 + 169 AL2 + 1.15 CA	0.73
	= 4.10 + 99.2 AL2 + 0.932 CLAY	0.91
	= 14.1 + 55.6 FE2 + 148 AL2	0.67
	= 9.29 - 1.15 CA + 1.61 CLAY	0.81
KF	= 3.58 + 2.52 FE1 + 2.29 AL1	0.53
	= 3.59 + 2.65 FE1 + 0.016 CA	0.53
	= 3.41 + 1.44 FE1 + 0.0270 CLAY	0.68
	= 3.83 + 6.24 AL1 + 0.0160 CA	0.12
	= 3.40 - 0.000123 AL1 + 0.0461 CLAY	0.60
	= 3.78 + 6.46 FE2 + 0.0140 CA	0.28
	= 3.36 + 3.18 FE2 + 0.0399 CLAY	0.66
	= 3.42 + 6.00 AL2 + 0.0251 CA	0.61
	= 3.24 + 4.41 AL2 + 0.0218 CLAY	0.79
	= 3.51 + 2.17 FE2 + 5.24 AL2	0.60
	= 3.50 - 0.0733 CA + 0.0545 CLAY	0.69
NF	= 0.564 - 0.038 FE1 - 0.288 AL1	0.01
	= 0.506 - 0.0591 FE1 + 0.00974 CA	0.09
	= 0.544 - 0.262 FE1 + 0.00438 CLAY	0.05
	= 0.514 - 0.404 AL1 + 0.00986 CA	0.10
	= 0.566 - 0.565 AL1 + 0.00157 CLAY	0.02
	= 0.477 + 0.291 FE2 + 0.00951 CA	0.10
	= 0.537 + 0.517 FE2 - 0.000119 CLAY	0.04
	= 0.495 - 0.0121 AL2 + 0.00969 CA	0.09
	= 0.559 - 0.371 AL2 + 0.00296 CLAY	0.03
	= 0.534 + 0.493 FE2 - 0.194 AL2	0.03
	= 0.510 + 0.0278 CA - 0.00227 CLAY	0.26
NFI	= 1.96 + 0.363 FE1 + 0.588 AL1	0.03
	= 2.16 + 0.412 FE1 - 0.0364 CA	0.14
	= 2.08 + 0.998 FE1 - 0.0141 CLAY	0.07
	= 2.17 + 1.37 AL1 - 0.0367 CA	0.12
	= 2.04 + 1.05 AL1 - 0.00210 CLAY	0.01
	= 2.30 - 1.07 FE2 - 0.0355 CA	0.13
	= 2.11 - 1.90 FE2 + 0.00289 CLAY	0.04
	= 2.18 + 0.511 AL2 - 0.0356 CA	0.12
	= 2.03 + 1.34 AL2 - 0.00826 CLAY	0.03
	= 2.05 - 2.34 FE2 + 1.35 AL2	0.07
	= 2.19 - 0.0845 CA + 0.00877 CLAY	0.23

equations. Because of this small difference and in order to keep input parameters at a minimum, we chose the two-property estimator equations over the three-property equations. However, we further evaluated the one-property equations (Tables V-10a-d).

Correlations using one-property equations to estimate model constants showed that FE1, AL2, FEAL1, FEAL2, and CLAY provided better estimates (Tables V10a-d). FE2 and AL1 were included in a more systematic analysis. The R^2 values showed generally that FE2 and AL1 were least desirable properties to use. This was somewhat surprising, since oxalate extractable Fe (FE2) had been shown to be strongly correlated with Langmuir phosphate sorption parameters (Berkheiser et al., 1980). Perhaps the Fe extraction method did not uniformly extract Fe. Differences in mineralogy of Fe containing minerals may account for the variability. The citrate-dithionite-Fe extraction, however, was better correlated to the sorption parameters than the oxalate extractable Fe, probably as a reflection of the reduction reaction which occurs during the extraction process.

For use in a model to calculate adsorption isotherms, regression equations from Tables V-10a and V-10c were used which had R^2 values of 0.5 or larger for both constants (sorption parameters) in the model equation. Thus, FE1, AL2, FEAL1, FEAL2, and CLAY were chosen as one-property estimators for the sorption parameters for the Temkin and Langmuir 2 equations (even though the isotherm fits to Langmuir 2 were unsatisfactory). Two-property estimator equations were chosen in the same manner from those listed in Tables V-11a and V-11b except that the minimum allowable R^2 was 0.8. As a result, FE1 and CLAY, FE2 and CLAY, AL2 and CLAY, and CA and CLAY were selected as two-property estimators using the Temkin equation. The pairs of properties turned out to be the same for estimating sorption parameters from KCl and $CaCl_2$ electrolytes. These equations were then used to calculate a sorption isotherm for each soil within its electrolyte group.

Additional linear regressions were performed separately by pooling all the $CaCl_2$ or KCl sorption data, in order to confirm the results of previous regressions, according to the model

$$S = (a_0 + a_1M_i + a_2CLAY + b_0 + b_1M_i + b_2CLAY)\ln C$$

where a_0, a_1, a_2, b_0, b_1, and b_2 are linear regression estimates and M_i represents either FE1, FE_2, AL_2, or CA. These M_i were chosen as a result of the regression analyses performed in the previous section. Results of these analyses are presented in Table V-13.

In general, the results presented for the correlations on pooled data (Table V-13) correspond to the results for correlations in which the Temkin constants were estimated separately (Table 11a and V-11b). For example the properties AL2 and CLAY or CA and CLAY gave the best R^2 values in both cases. The Freundlich model was not used further because the parameter N could not be estimated within necessary limits (R^2 was only 0.50 for the best case in all regressions performed, Tables V-11a and V-11b).

Table V-12. Linear regressions correlation coefficient (R^2) matrix between soil properties.

Dependent variable	Independent variable					
	FE1	AL1	FE2	AL2	CA	CLAY
FE1	1.00	0.04	0.19	0.68	0.005	0.51
AL1	0.04	1.00	0.0005	0.01	0.001	0.01
FE2	0.19	0.0005	1.00	0.25	0.01	0.14
AL2	0.68	0.01	0.25	1.00	0.02	0.33
CA	0.005	0.001	0.01	0.02	1.00	0.12
CLAY	0.51	0.01	0.14	0.33	0.12	1.00

Table V-13. Phosphate sorption prediction equations resulting from multiple linear regression on pooled data for KCl and $CaCl_2$ electrolytes using the two-property Temkin model.

Electrolyte	Equation	R^2
KCl	$S = 30.8 + 270\ \mathrm{FE1} + 4.24\ \mathrm{CLAY} + (9.25 + 38.4\ \mathrm{FE1} + 0.711\ \mathrm{CLAY})\ln C$	0.82
	$= -54.7 + 420\ \mathrm{FE2} + 7.29\ \mathrm{CLAY} + (8.56 + 94.5\ \mathrm{FE2} + 1.04\ \mathrm{CLAY})\ln C$	0.72
	$= -76.8 + 530\ \mathrm{AL2} + 5.62\ \mathrm{CLAY} + (2.50 + 67.2\ \mathrm{AL2} + 1.02\ \mathrm{CLAY})\ln C$	0.85
	$= -18.5 - 13.2\ \mathrm{CA} + 9.90\ \mathrm{CLAY} + (13.6 - 2.67\ \mathrm{CA} + 1.65\ \mathrm{CLAY})\ln C$	0.84
$CaCl_2$	$S = 2.16 + 216\ \mathrm{FE1} + 4.82\ \mathrm{CLAY} + (8.53 + 33.8\ \mathrm{FE1} + 0.902\ \mathrm{CLAY})\ln C$	0.79
	$= -2.51 + 426\ \mathrm{FE2} + 6.66\ \mathrm{CLAY} + (8.70 + 96.9\ \mathrm{FE2} + 1.09\ \mathrm{CLAY})\ln C$	0.76
	$= -17.3 + 540\ \mathrm{AL2} + 4.69\ \mathrm{CLAY} + (5.30 + 88.7\ \mathrm{AL2} + 0.866\ \mathrm{CLAY})\ln c$	0.84
	$= 15.9 - 13.2\ \mathrm{CA} + 9.60\ \mathrm{CLAY} + (8.08 - 1.07\ \mathrm{CA} + 1.66\ \mathrm{CLAY})\ln C$	0.85

The regression coefficients were similar for the two analyses. The latter method using pooled data is probably more statistically correct since the model is the one by which the sorption isotherms were originally linearized.

In order to test for correlation between soil properties, a linear regression analysis was conducted. These results are summarized in Table V-12. Highest correlations occurred between FE1 and AL2 ($R^2 = 0.68$), FE1 and CLAY ($R^2 = 0.51$), and AL_2 and CLAY ($R^2 = 0.33$). Thus, it is not surprising that FE1, AL2, and CLAY consistently appeared together in the regression analyses, and probably reflected the coexistence of the metals in structurally similar minerals.

Sorption isotherms were calculated using the best two equations from Table V-13 (by R^2) for each electrolyte in order to compare with observed isotherms. Confidence intervals at the 95% level were calculated for individual soils using a propogation of errors technique (Berkheiser et al., 1980) according to the equations listed in Table V-14. The equations listed allow the variance of variance of S, σ_s^2, to be computed; the 95% confidence interval was given as $\pm 2\sqrt{\sigma_s^2}$ about any value of S for a given isotherm. An example of these computations is shown in Fig. V-4 for Grenada Ap using either oxalate-Al and clay or ammonium acetate-Ca and clay for two-property estimates of Temkin coefficients and compared with the sorption isotherm obtained in $CaCl_2$ electrolyte.

The results for Grenada soil indicate that oxalate-Al and clay content provide a better estimate of predicted phosphate sorption than using ammonium acetate-Ca and clay as soil properties. However, predicted isotherms and confidence intervals from all soils show that ammonium acetate-Ca and clay are more useful. A criterion for determining the usefulness of a particular model would be that if a part or all of the observed isotherm lies within the 95% confidence limits of the calculated isotherm then that particular model is useful. Based on this criterion, the observed isotherms of each soil and the confidence limits from each prediction equation (Table V-13) were compared. For the $CaCl_2$ electrolyte, AL2 and CLAY usefully predicted 15 of 25 isotherms, CA and CLAY usefully predicted 18 of 25 isotherms. Similar results were obtained for the KCl electrolyte: AL2 and CLAY usefully predicted 8 of 15 isotherms and CA and CLAY usefully predicted 10 of 15 isotherms.

Computation of isotherms for EPA Project soils deserves separate mention. Four of the six soils contain appreciable amounts of 2:1 expandable layer silicates, a fifth soil (Cecil) contains mineralogy typical of the highly weathered soils of the Southeast, and the sixth (Grenada) appears to be in between the other two groups mineralogically. The data in this project was derived mostly from soils of the Southeast (19 of 24 soils used in the correlations). Cecil, Grenada, Houston, and Webster soil phosphate sorption isotherms in KCl electrolyte were predicted within confidence limits by the model using Ca and clay as soil properties. Yolo phosphate sorption in KCl electrolyte was usefully modelled by oxalate-Al and clay but not by Ca and clay. Prediction of phosphate sorption in $CaCl_2$ electrolyte

Table V-14. Equations used to compute variance of s, σ_s^2, based on the Temkin model.*

Electrolyte	Equation
KCl Al2, clay	$\sigma_s^2 = 83.12 + 1218(AL2)^2 + (CLAY)^2(0.10) + [20.1 + 310(AL2)^2 + 0.03(CLAY)^2](\ln C)^2 + 6.73\ln C + (2.5 + 67.2\ AL2 + 1.02\ CLAY)^2(5 \times 10^{-5})/C^2$
Ca, clay	$\sigma_s^2 = 66.1 + 174(CA)^2 + 0.10(CLAY)^2 + 55.2 + [22.3 + 0.18(CA)^2 + 0.02(CLAY)^2](\ln C)^2 + 43.78\ln C + (13.6 - 2.67\ CA + 1.65\ CLAY)^2(5 \times 10^{-5})/C^2$
$CaCl_2$ Al2, clay	$\sigma_s^2 = 25.4 + 1050(AL2)^2 + 0.08(CLAY)^2 + 13.5 + [5.47 + + 207(AL2)^2 + 0.02(CLAY)^2](\ln C)^2 + 4.95\ \ln C + (5.3 + 88.7\ AL2 + 0.866\ CLAY)^2(5 \times 10^{-5})/C^2$
Ca, clay	$\sigma_s^2 = 23.9 + 0.63(CA)^2 + 0.06(CLAY)^2 + 51.9 + [6.17 + 0.12(CA)^2 + 0.01(CLAY)^2](\ln C)^2 + 17.93\ \ln C + (8.08 - 1.07\ CA + 1.66\ CLAY)^2(5 \times 10^{-5})/C^2.$

*Each soil property and the equilibrium concentration have associated variances as follows:

$$\sigma_{AL2}^2 = 4.0 \times 10^{-6}\text{(mmoles/100 g soil)}^2$$

$$\sigma_{CLAY}^2 = 0.56\ (\%)^2$$

$$\sigma_{CA}^2 = 2.25 \times 10^{-4}\text{(mmole/100 g soil)}^2$$

$$\sigma_C^2 = 2.50 \times 10^{-5}(\mu\text{g P/ml})^2$$

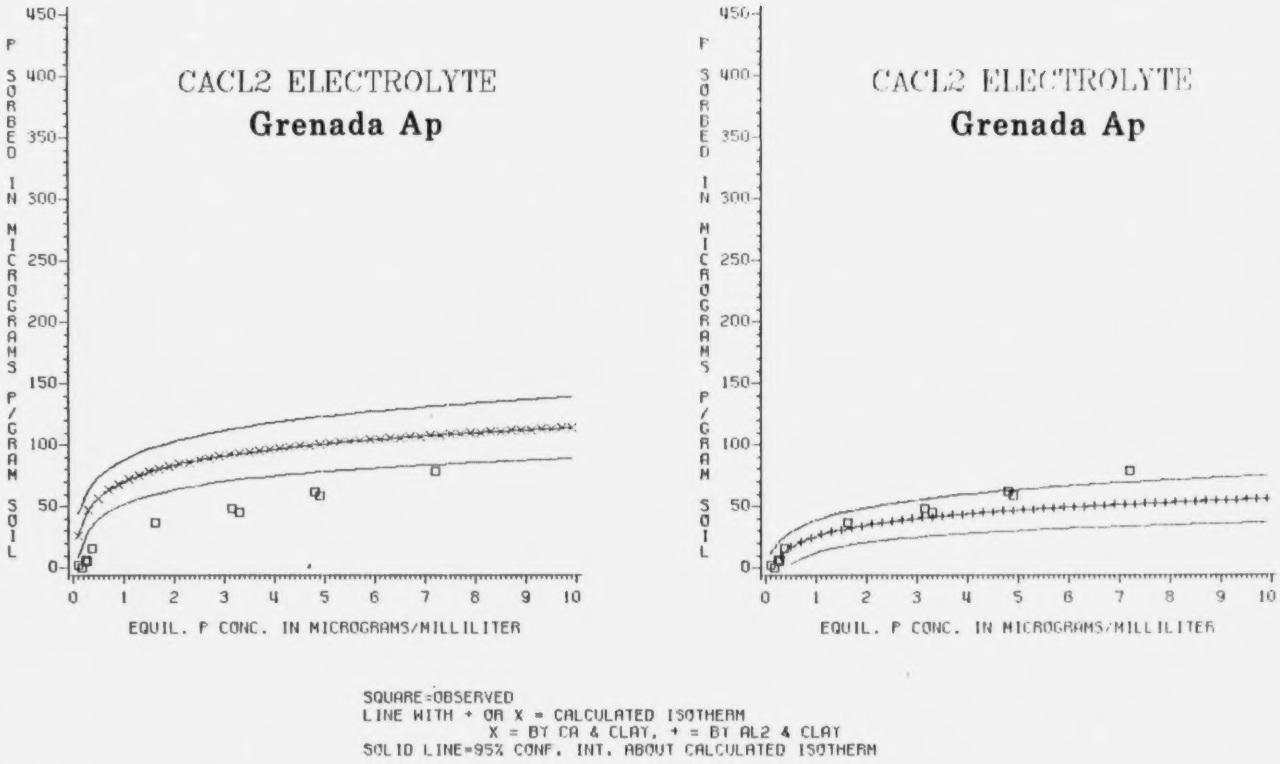

Figure V-4. Observed and Calculated P Sorption Isotherms for Grenada Soils.

was less useful than prediction of KCl data. Prediction of sorption by Sharpsburg was not successful by any model used here. We thus conclude that CA and CLAY are more useful soil properties from which isotherms could be calculated. Other judgement criteria which could have been used could include total standard deviation or variances between the observed and calculated isotherms, but were not computed. No common soil property appeared to be related to those isotherms which were not correctly predicted.

Our results allow computation of phosphate sorption with 72% of the computed isotherms lying within the 95% confidence limits calculated using properties from a wide range of soils. The confidence limits calculated in this report were based on variabilities in the analytical procedures used to measure soil properties and do not represent variabilities among soils. Therefore, by representing the computed variance associated with sorbed phosphate by the equations in Table V-14, we compute what would be expected to be a minimum variance σ_s^2 of sorbed phosphate. Because the individual components of each equation (soil property or equilibrium phosphate concentration) have low analytical variances (see footnote Table V-14), the confidence interval calculated on the basis of the Temkin equation would probably be less than the confidence interval calculated using the variance associated with variability among soils for each property.

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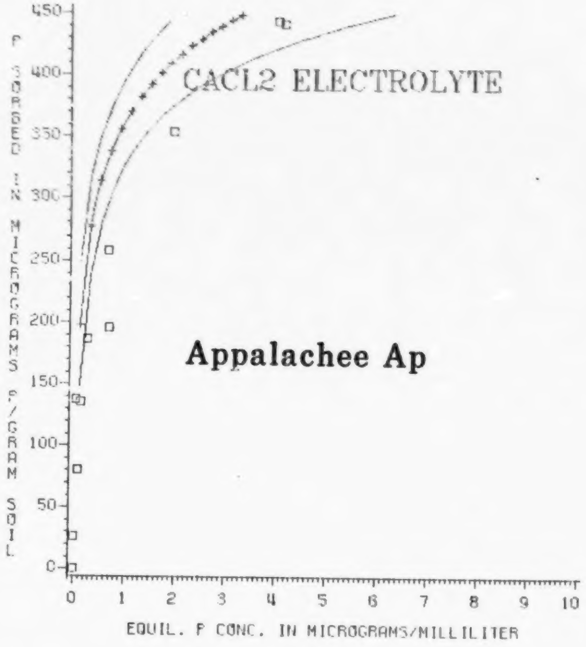
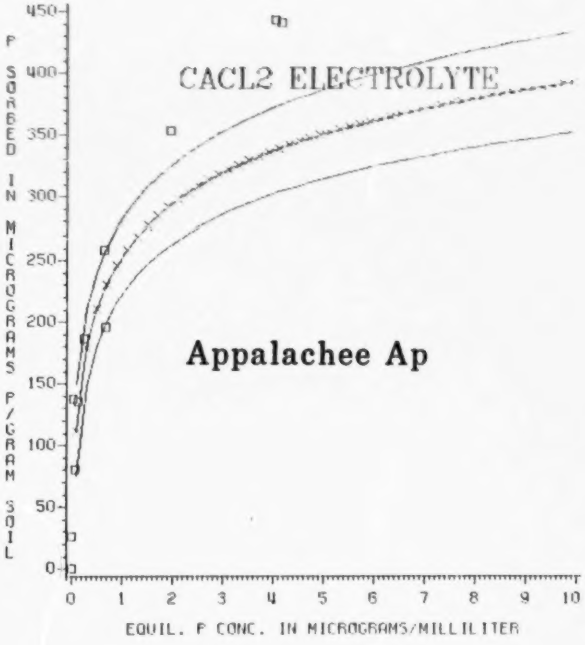
APPENDIX. PHOSPHORUS ADSORPTION DATA





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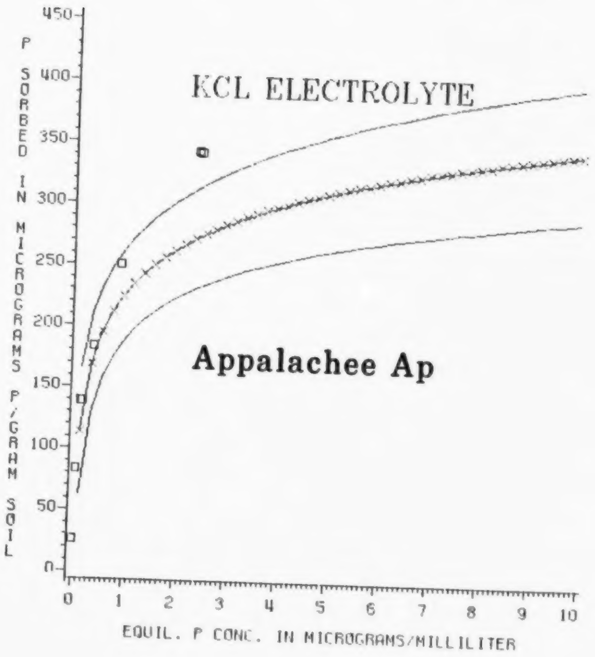

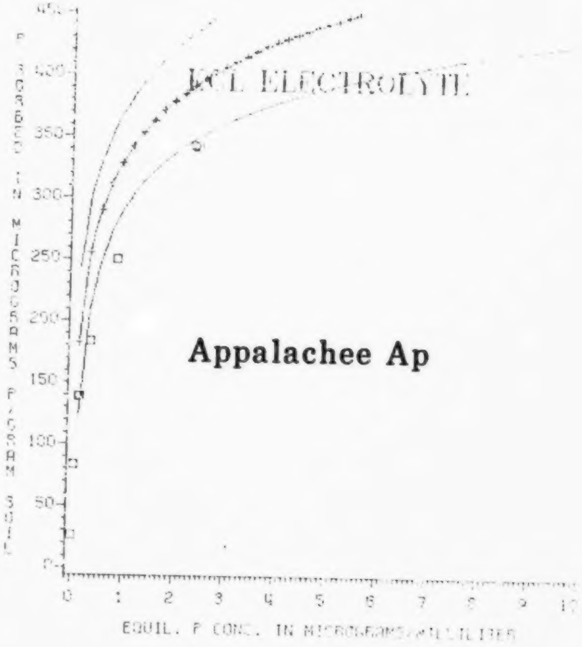

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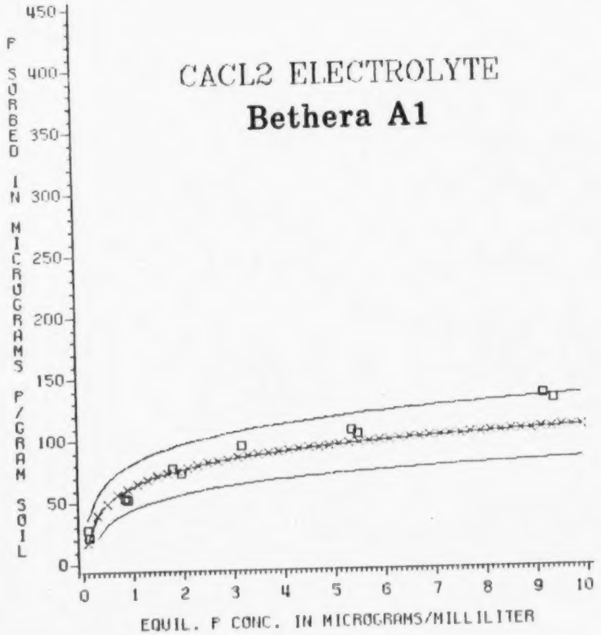

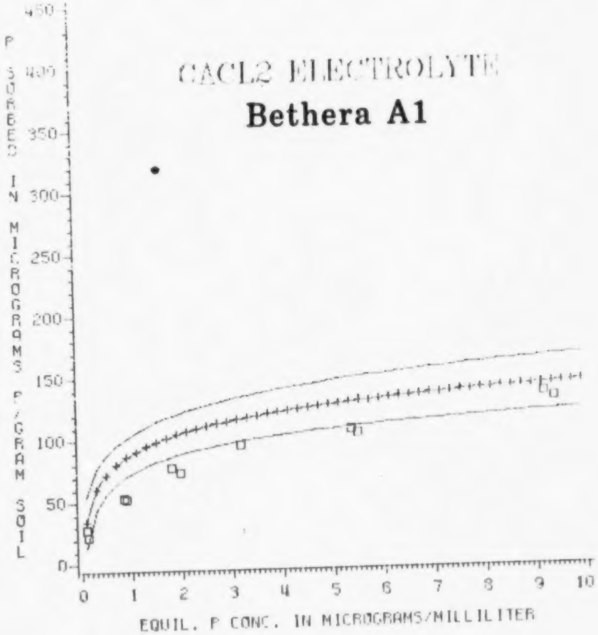

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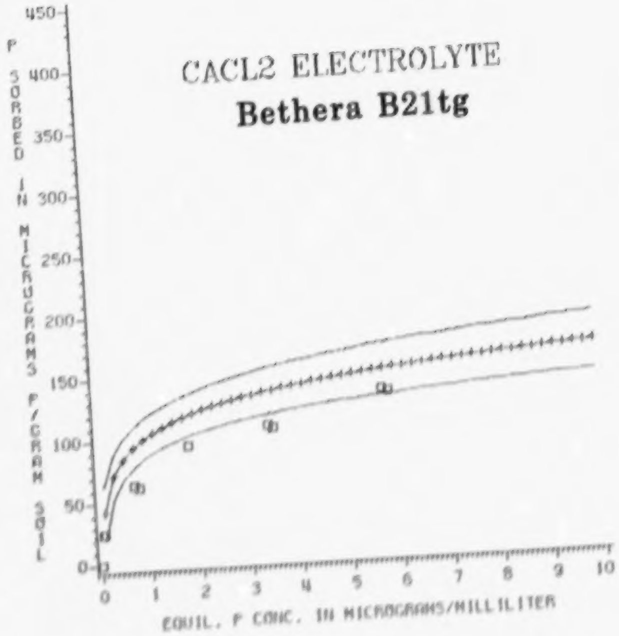

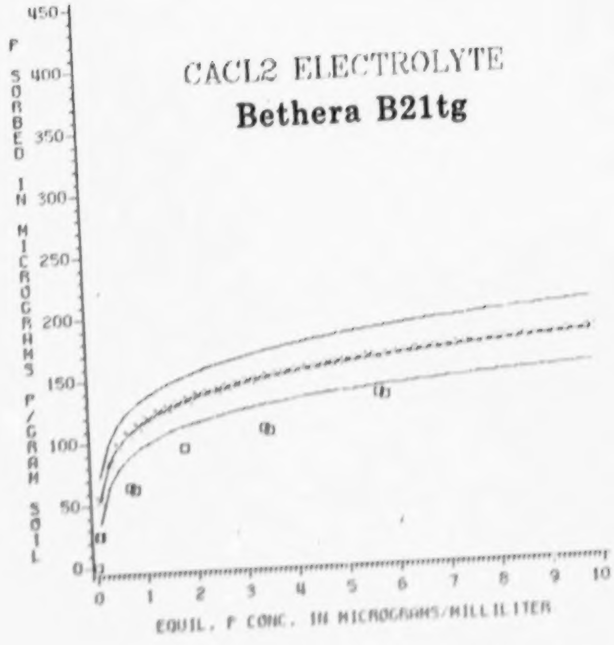

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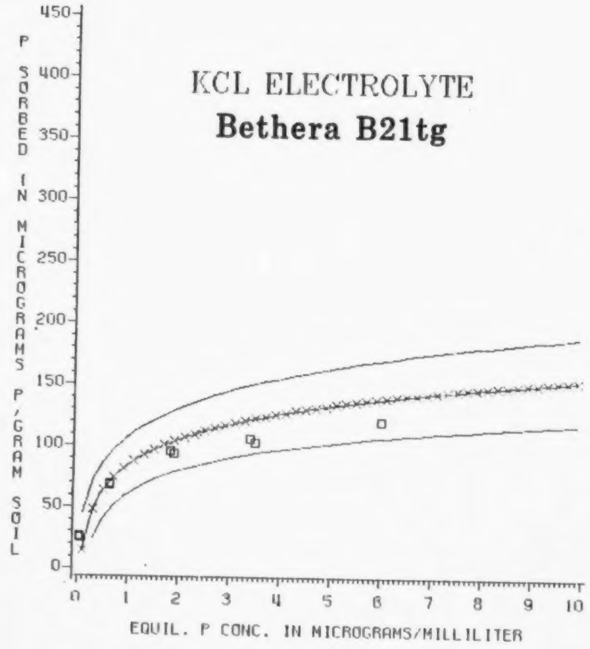

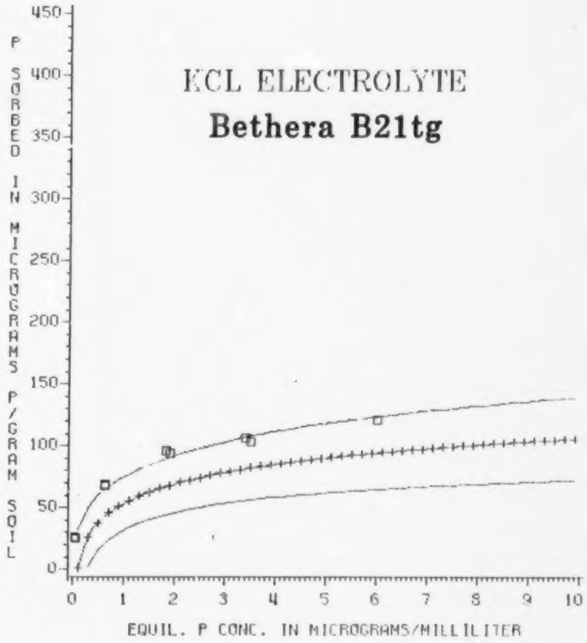

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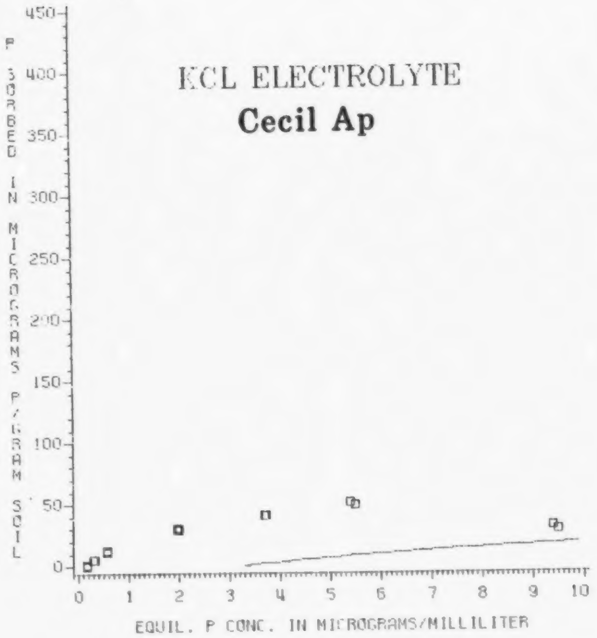

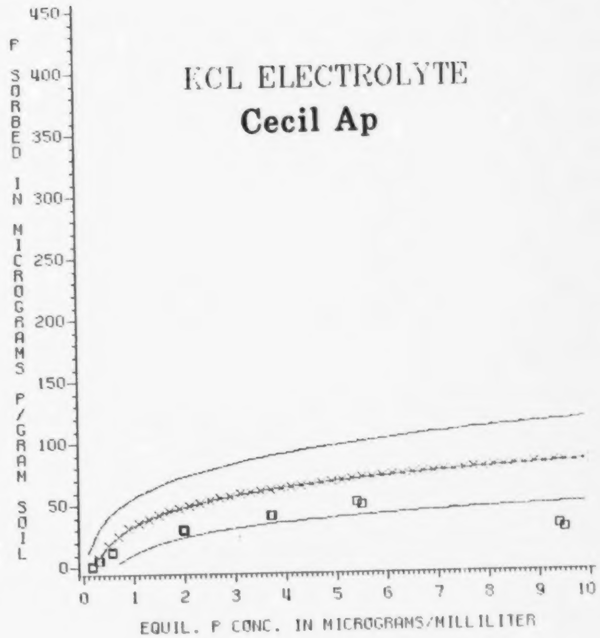

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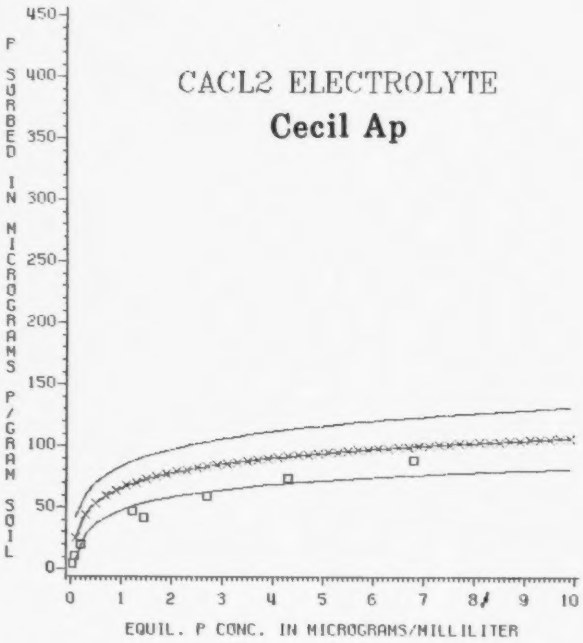

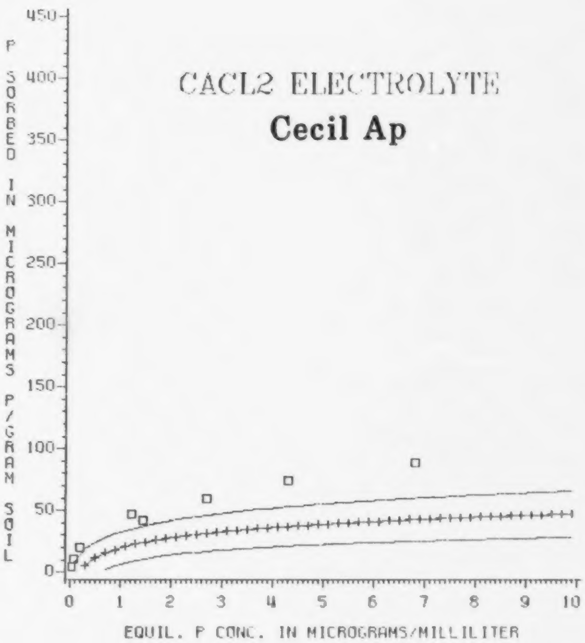

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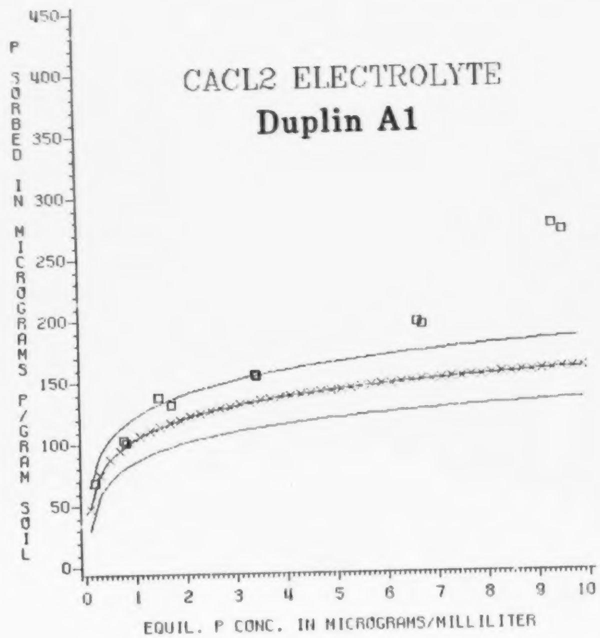

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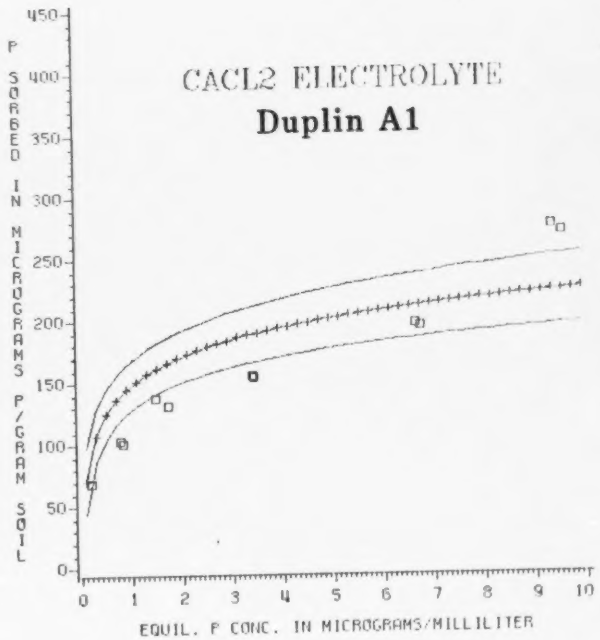

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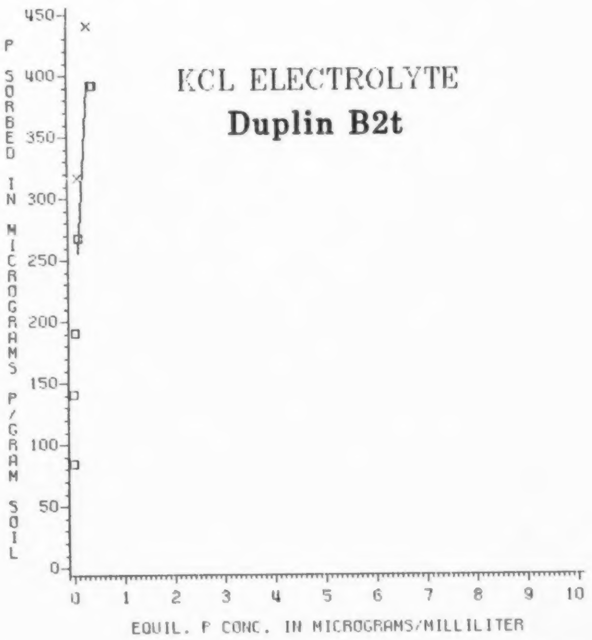
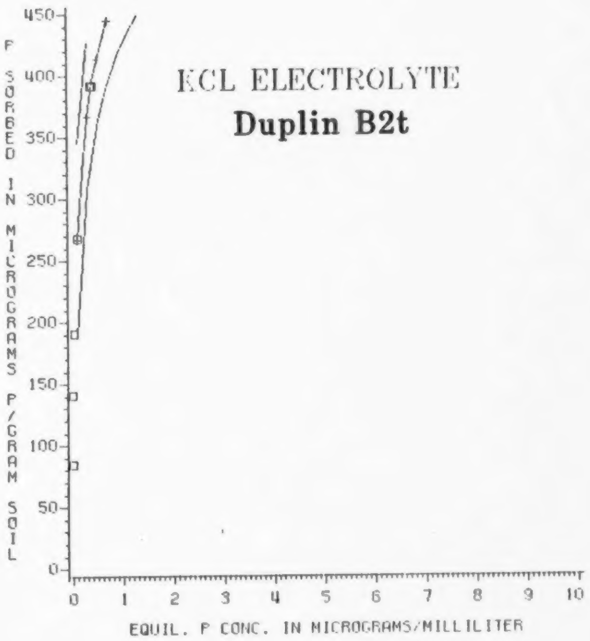
Duplin A1

SQUARE=OBSERVED
LINE WITH + OR X = CALCULATED ISOTHERM
X = BY CA & CLAY, + = BY AL2 & CLAY
SOLID LINE=95% CONF. INT. ABOUT CALCULATED ISOTHERM





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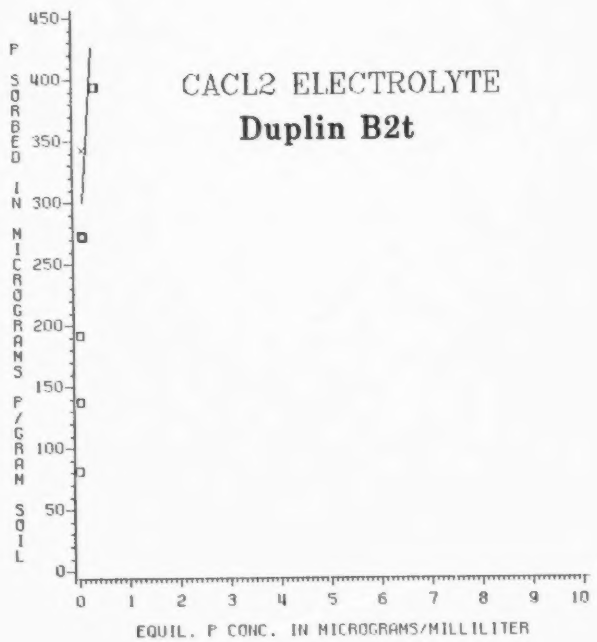

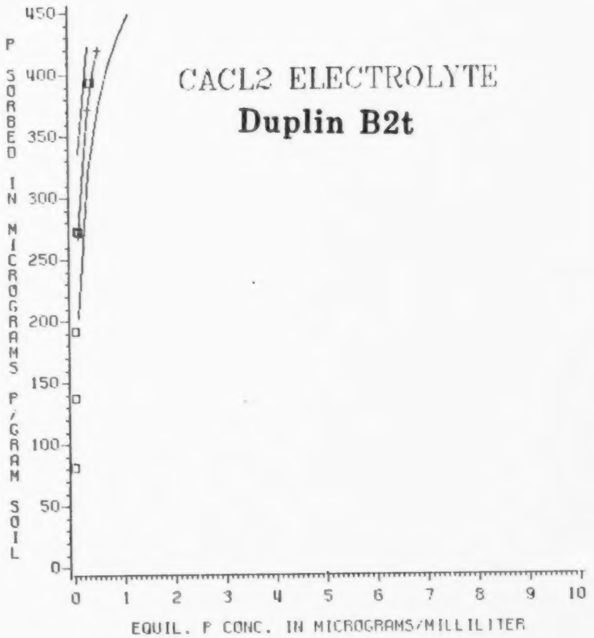

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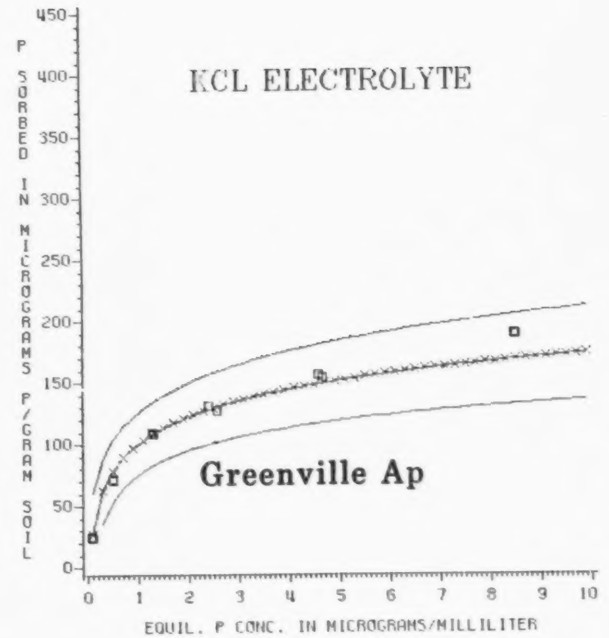

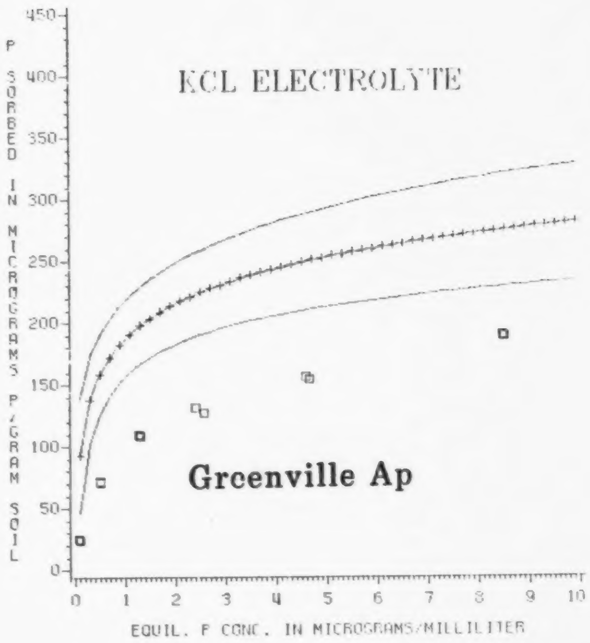

SQUARE=OBSERVED
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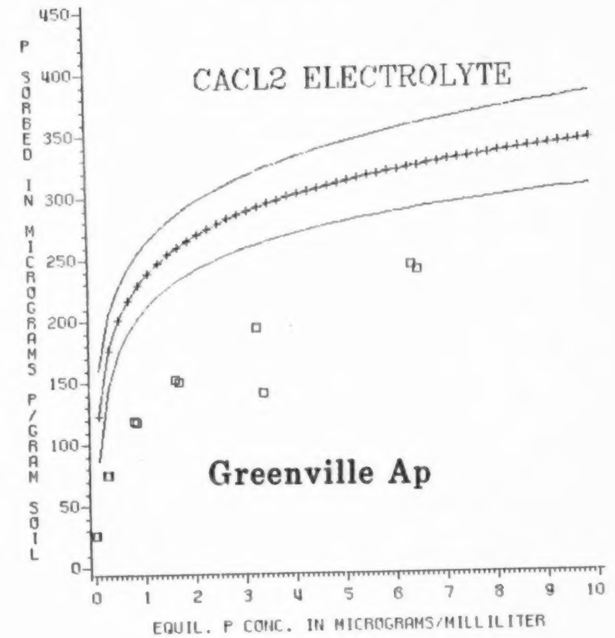

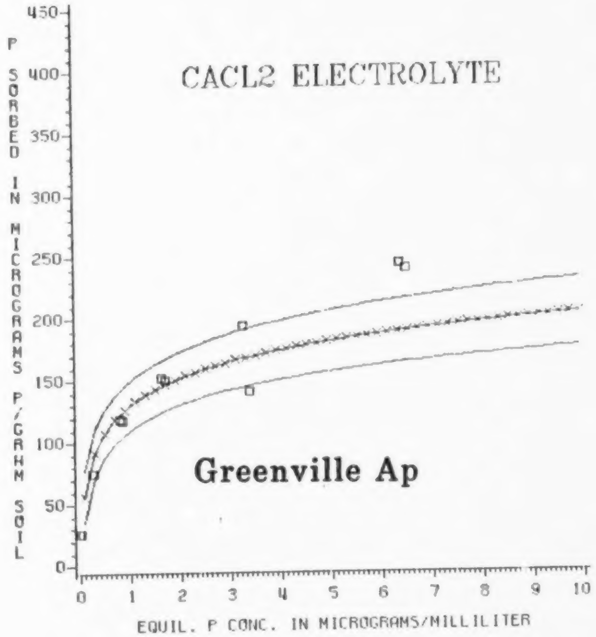

SQUARE=OBSERVED
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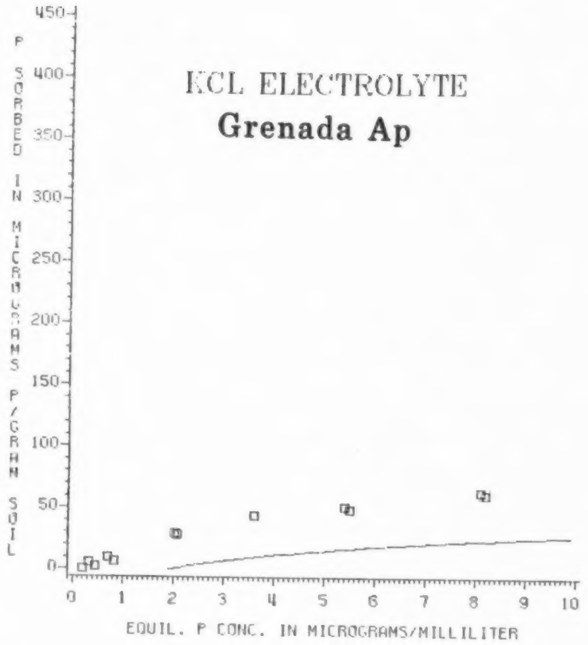
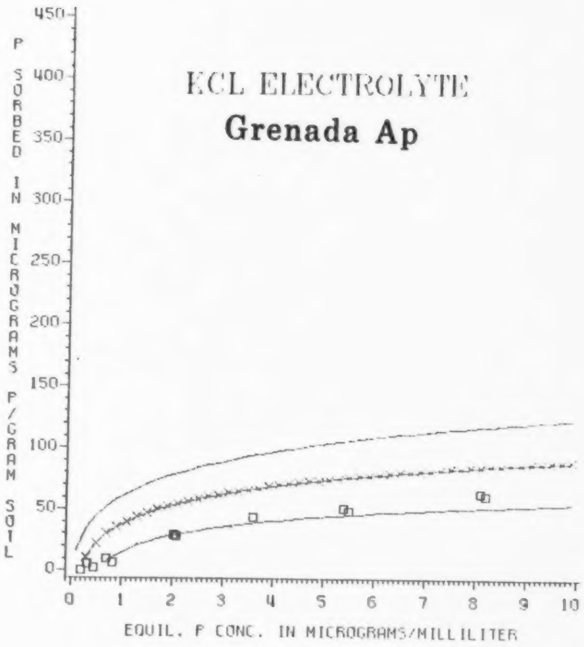
X = B1 CA & CLA1. + = B1 AL2 & CLA1
SOLID LINE=95% CONF. INT. ABOUT CALCULATED ISOTHERM





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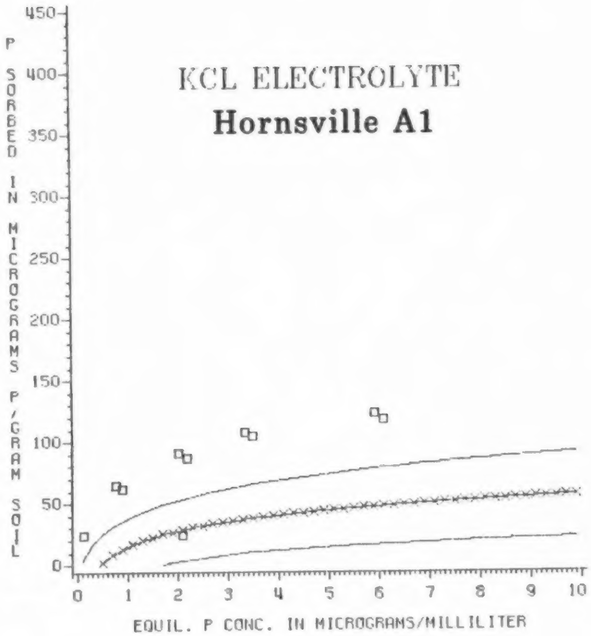

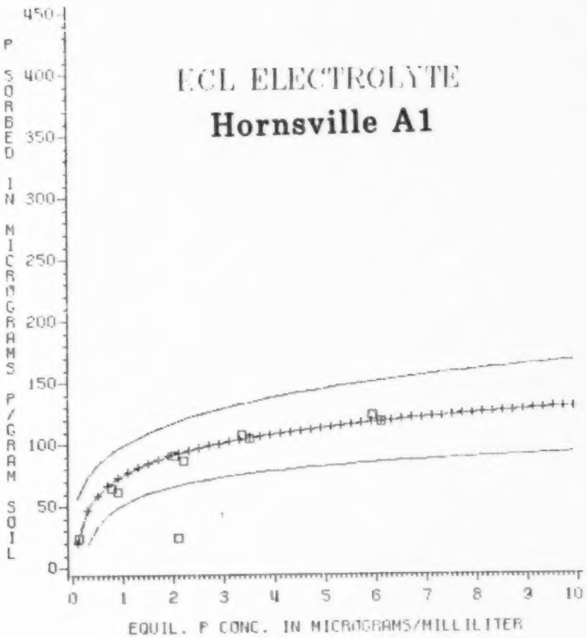

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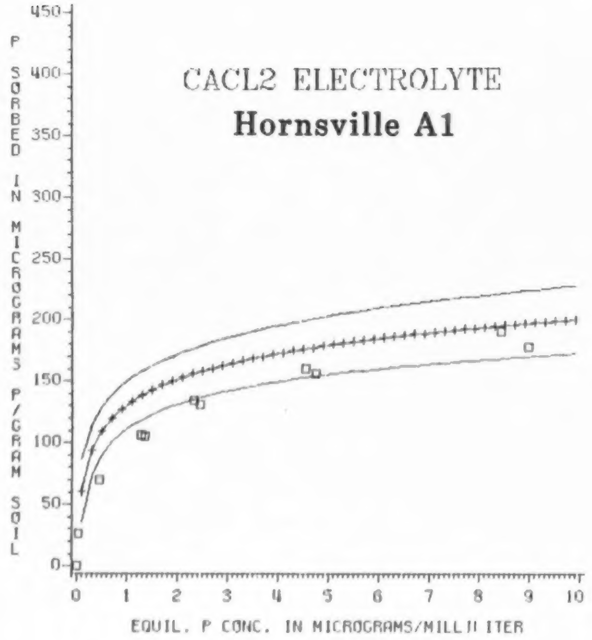

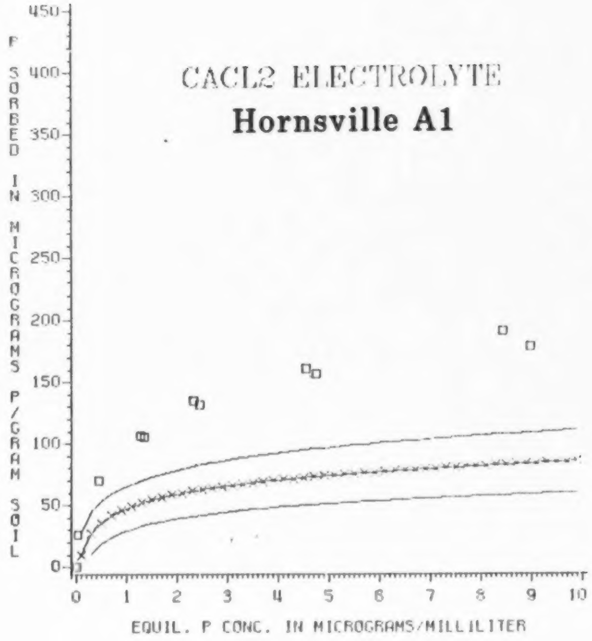

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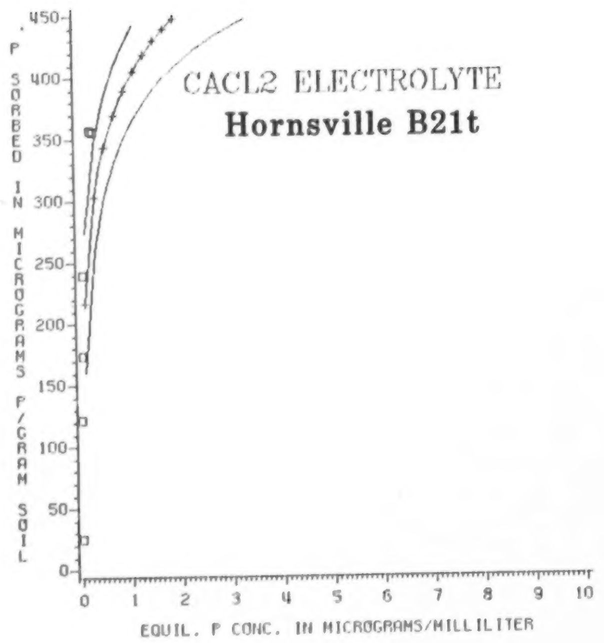

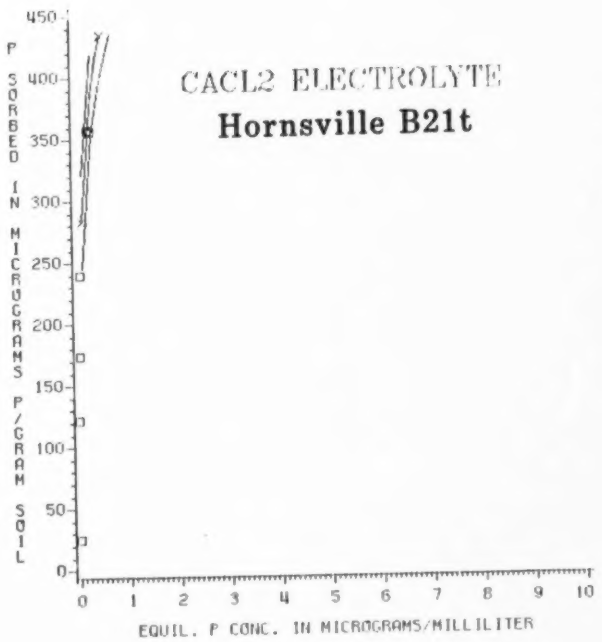

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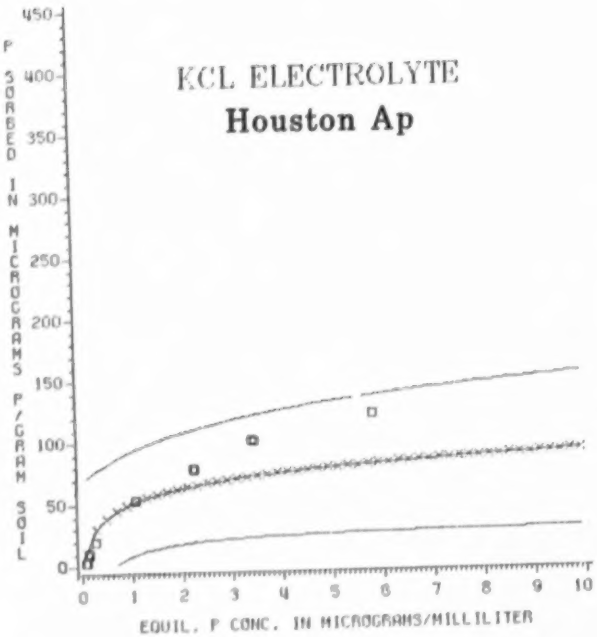

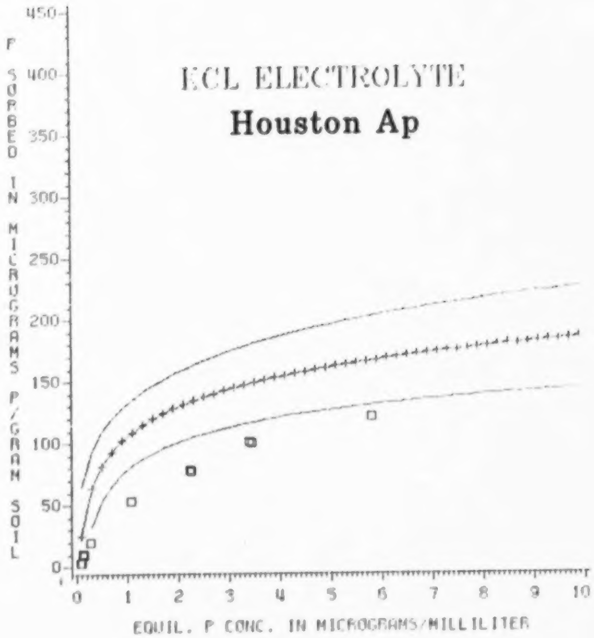

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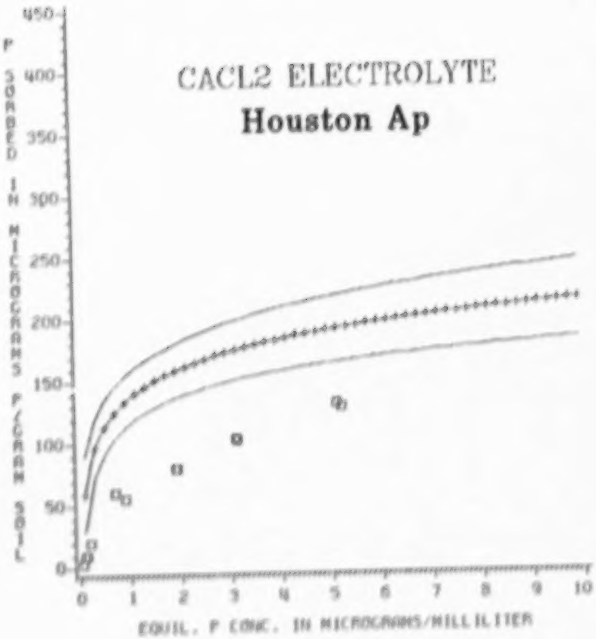

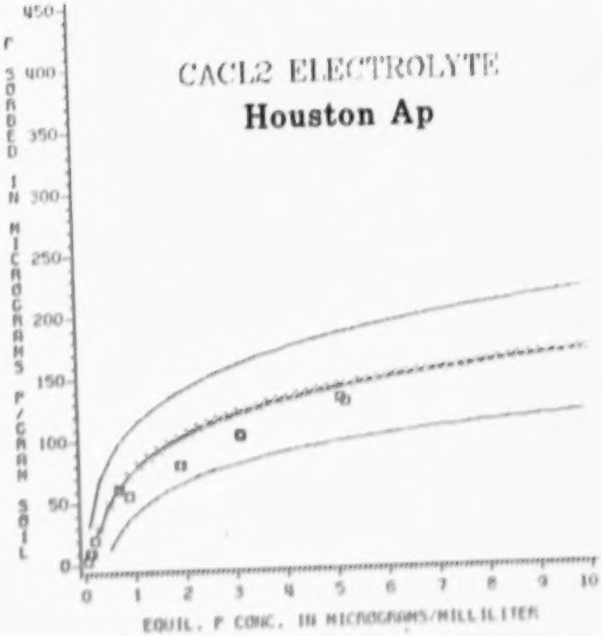

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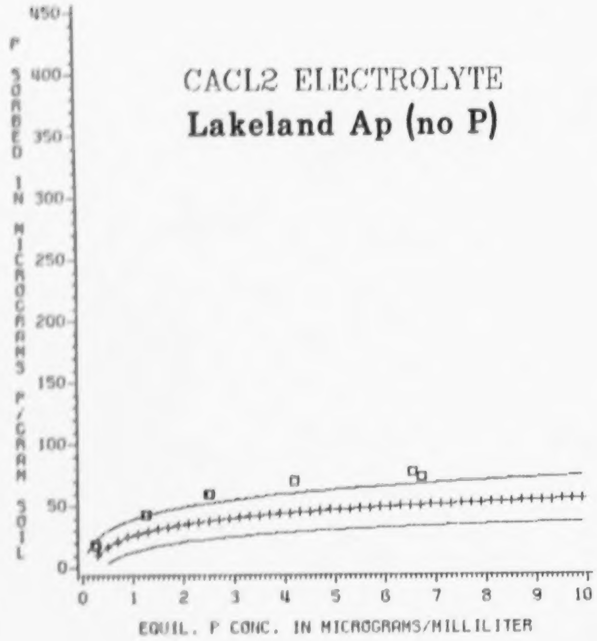

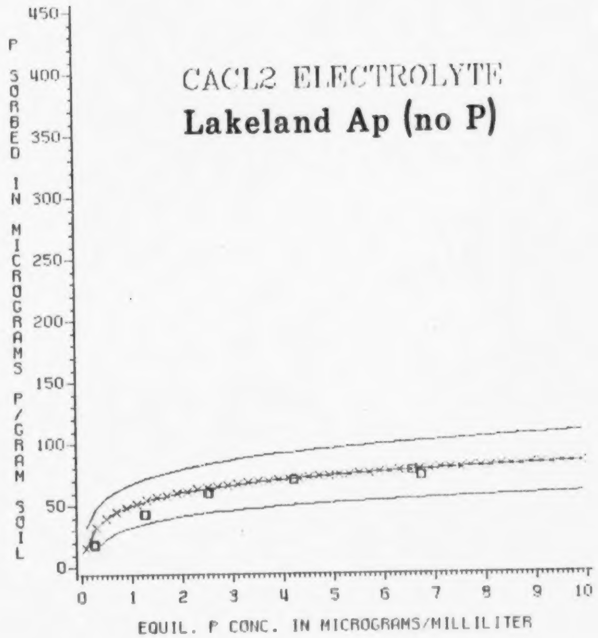

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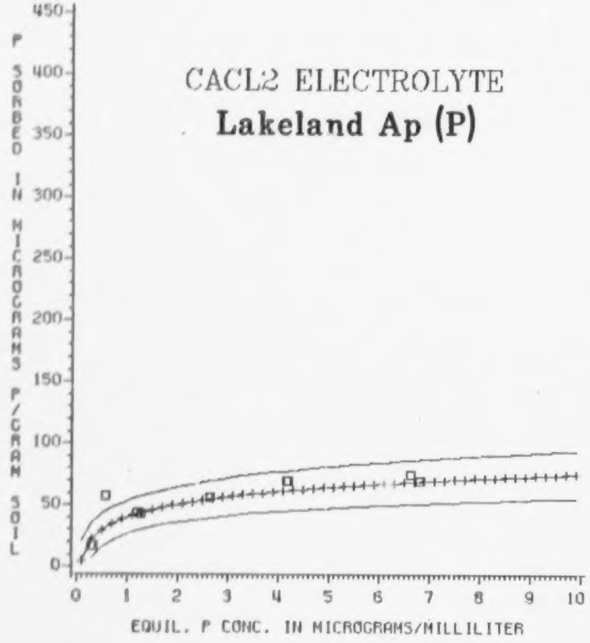

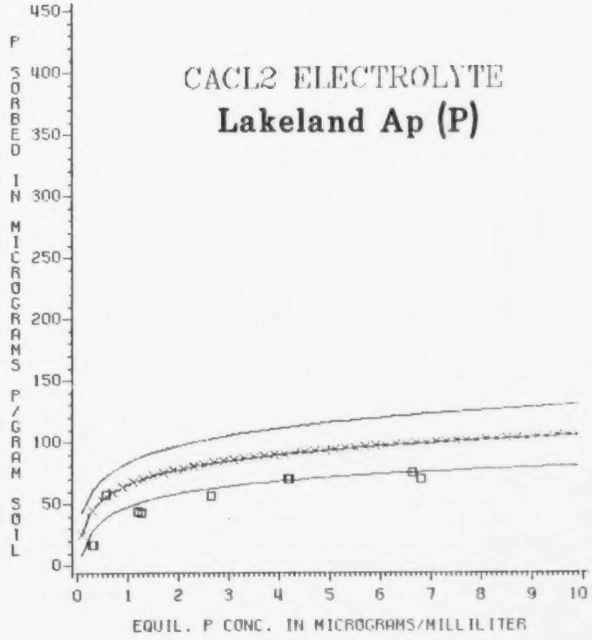

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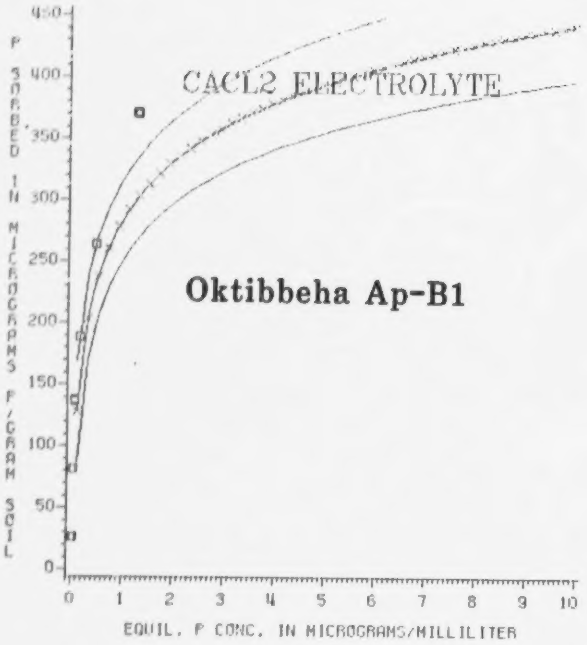

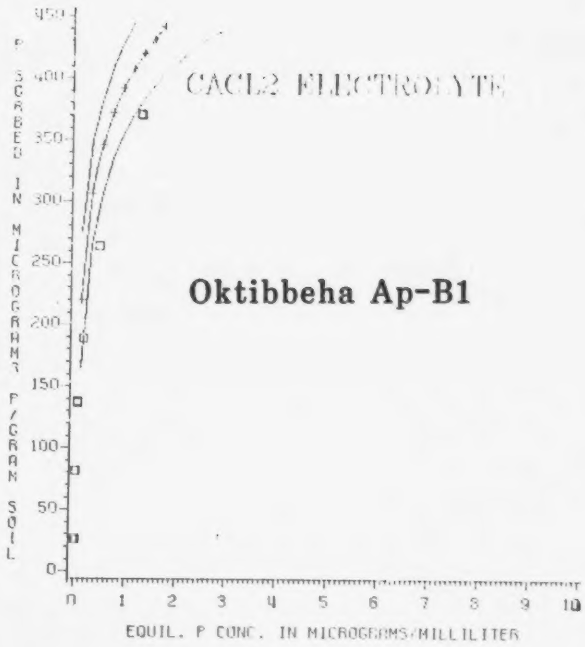

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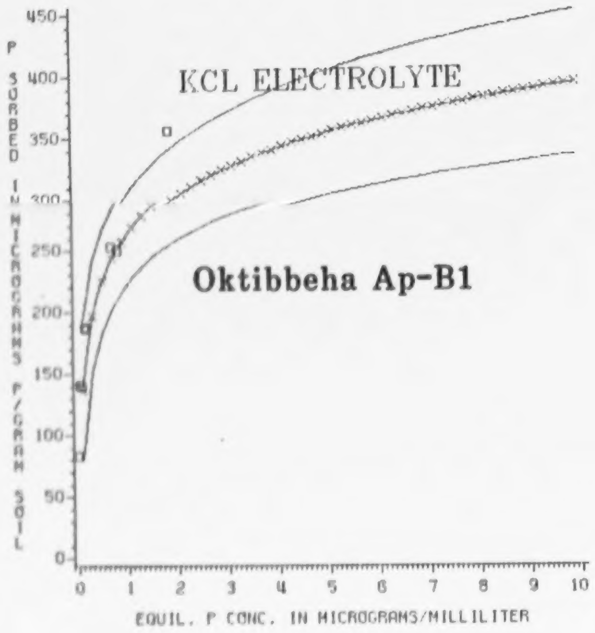

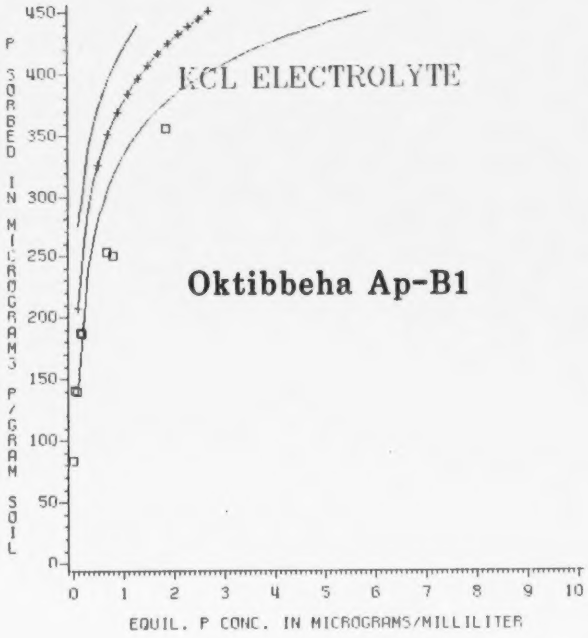

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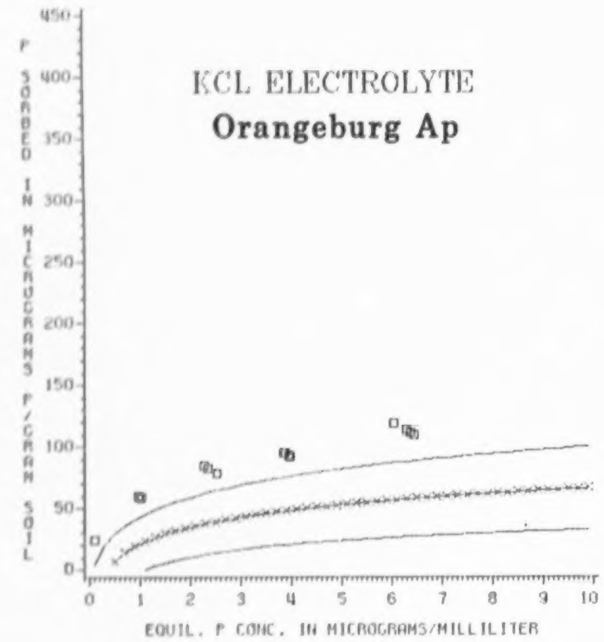

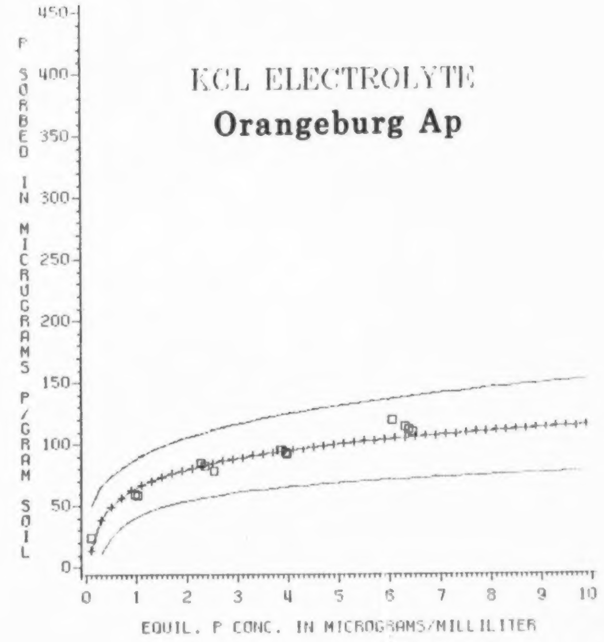

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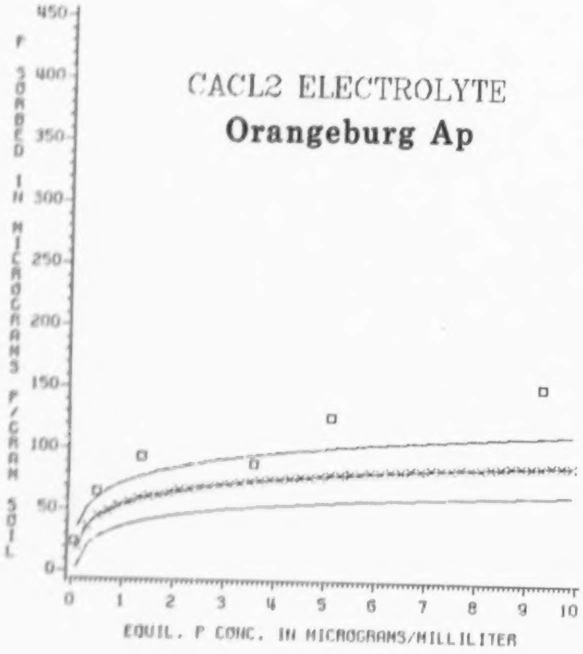

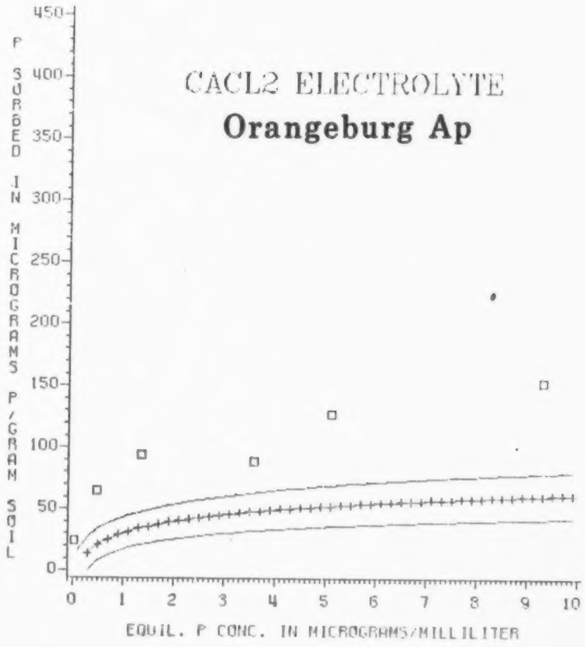

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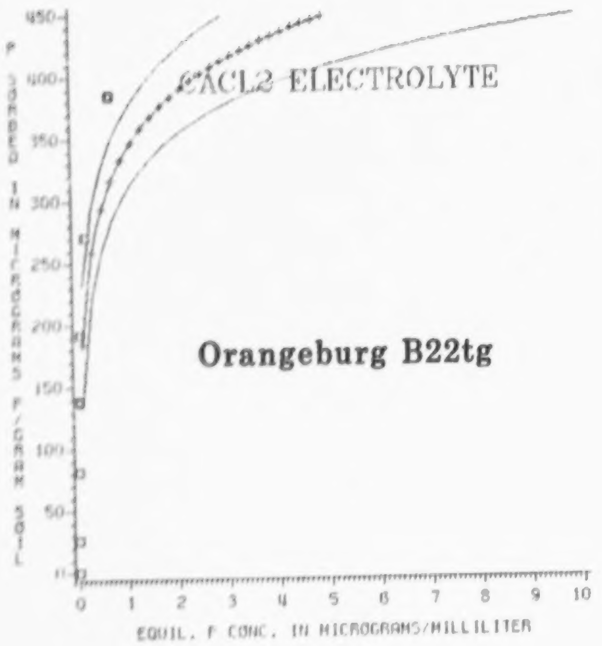

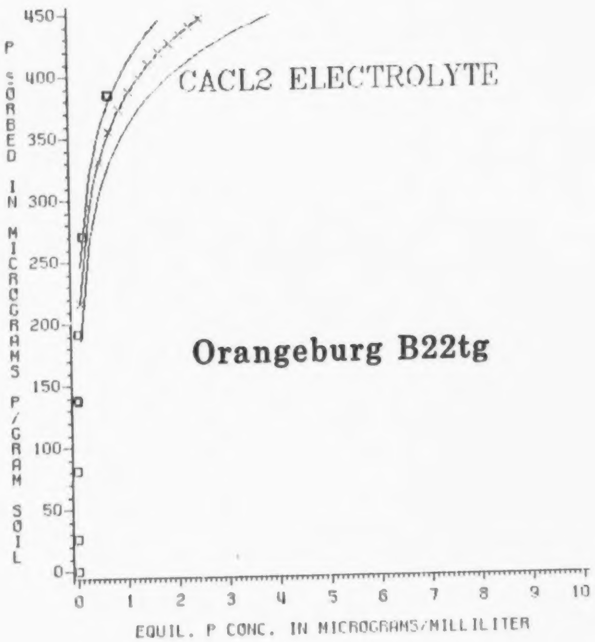

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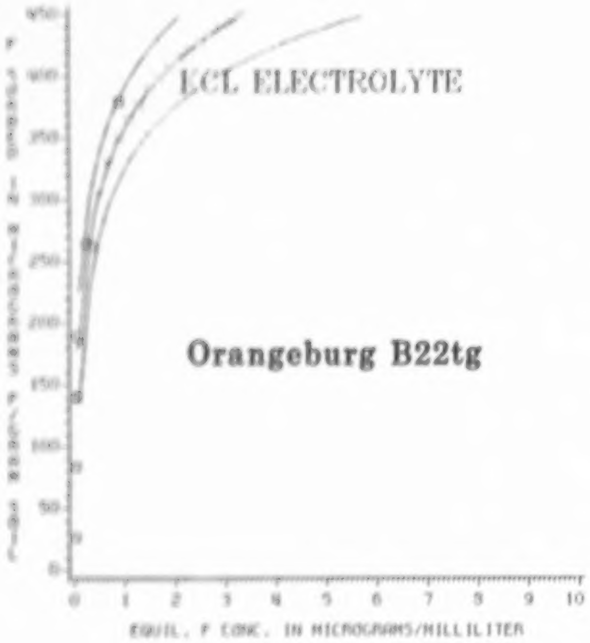

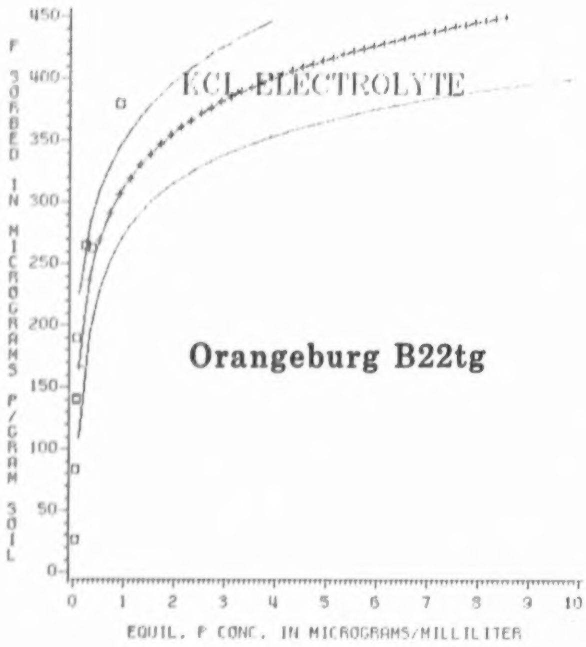

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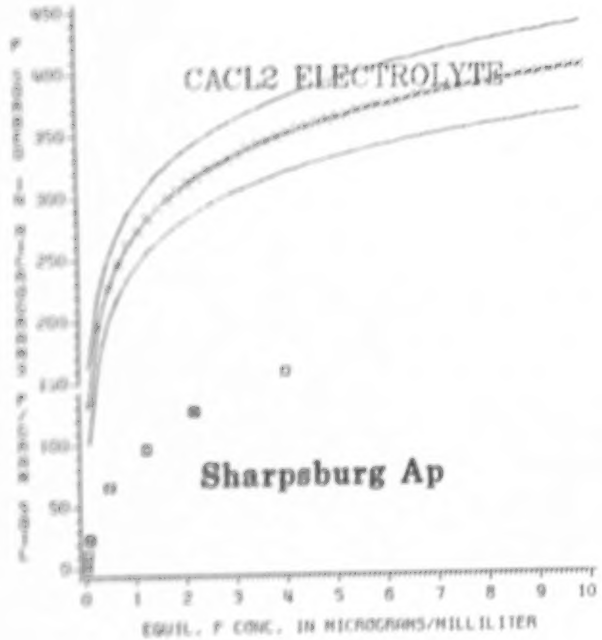

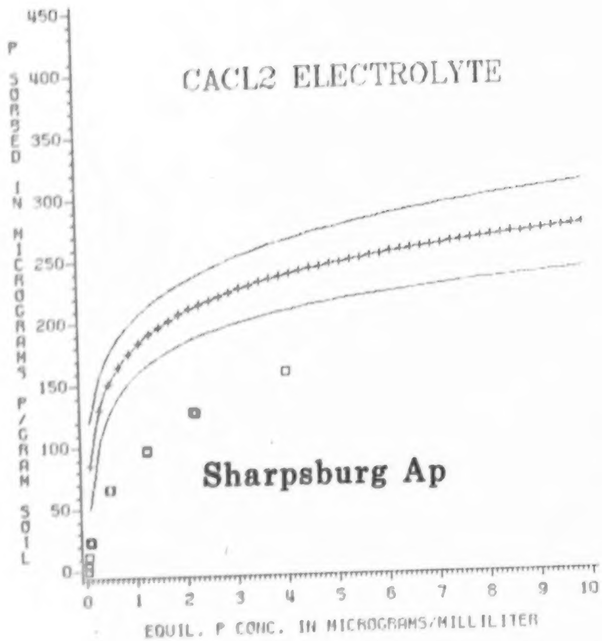

SQUARE=OBSERVED
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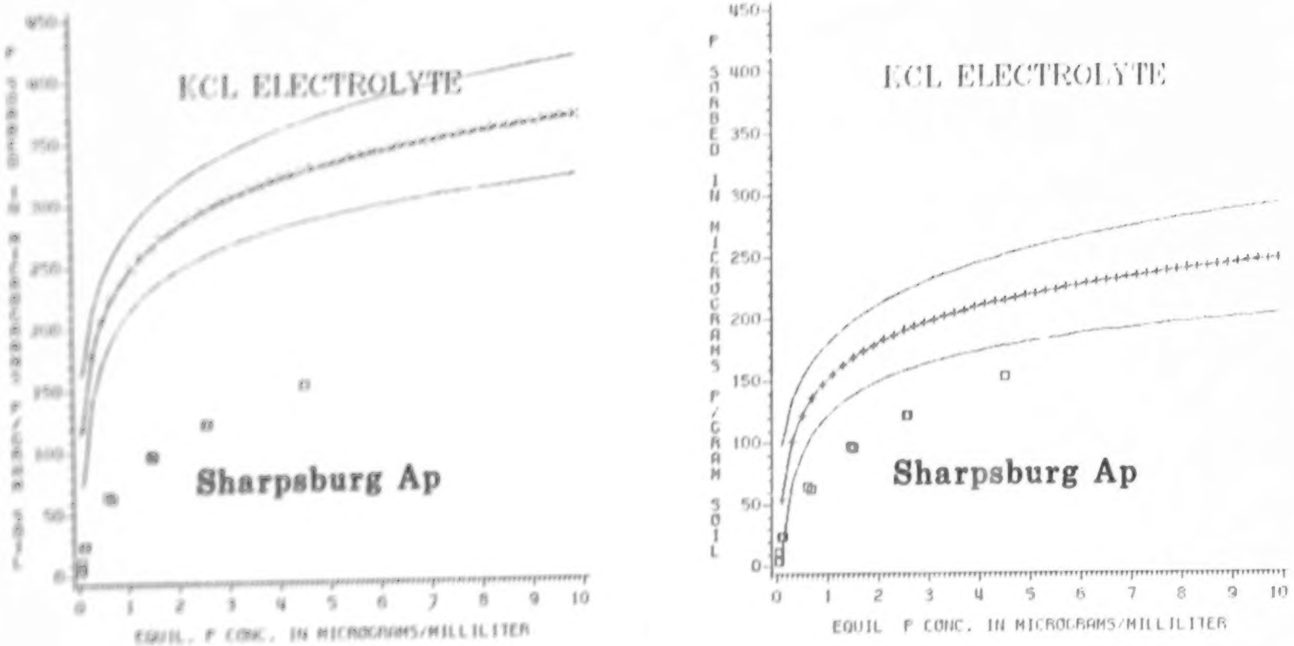
X = B1 CA & CLAY, + = B1 AL2 & CLAY
SOLID LINE=95% CONF. INT. ABOUT CALCULATED ISOTHERM



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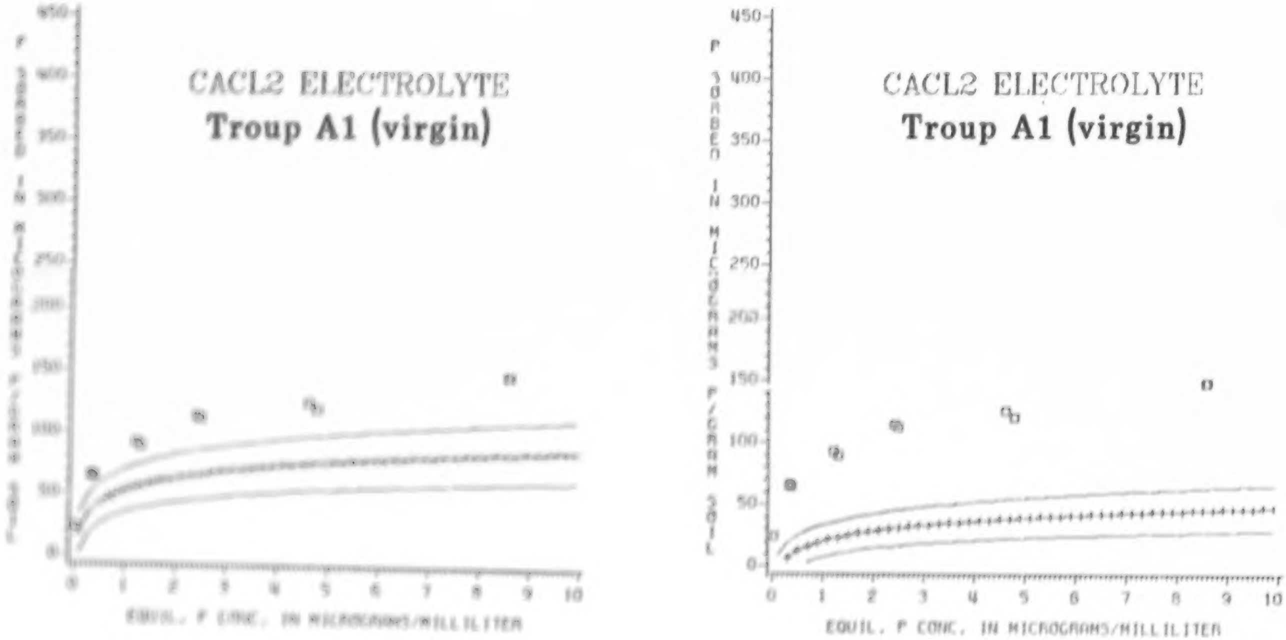

SQUARE=OBSERVED
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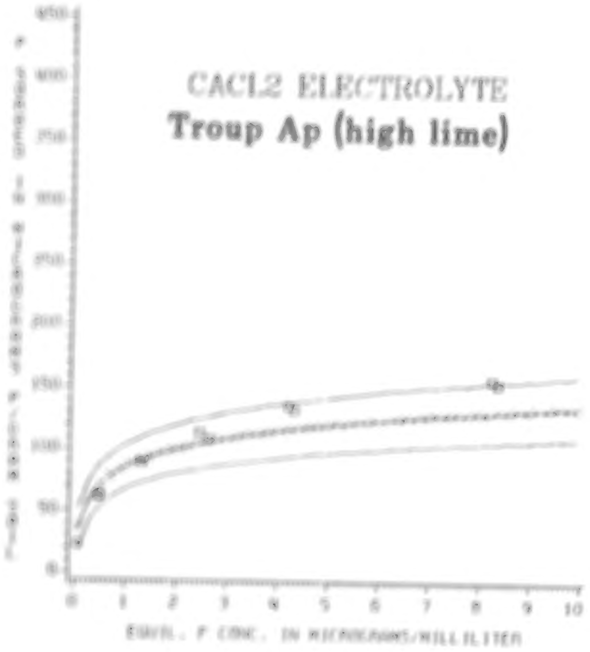
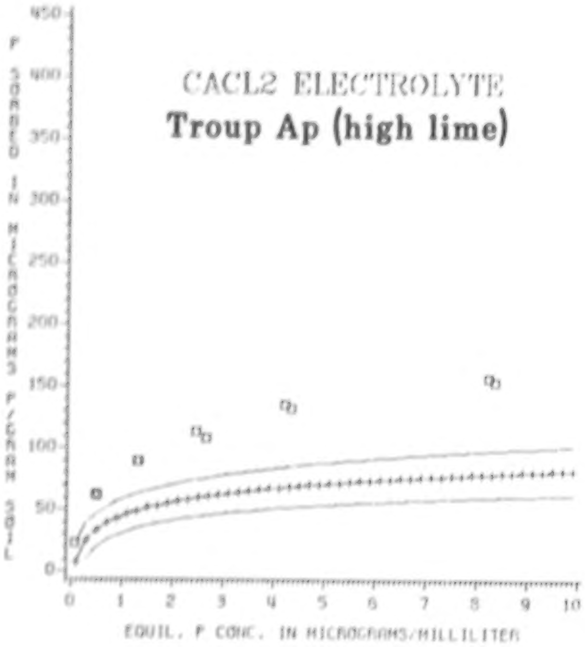
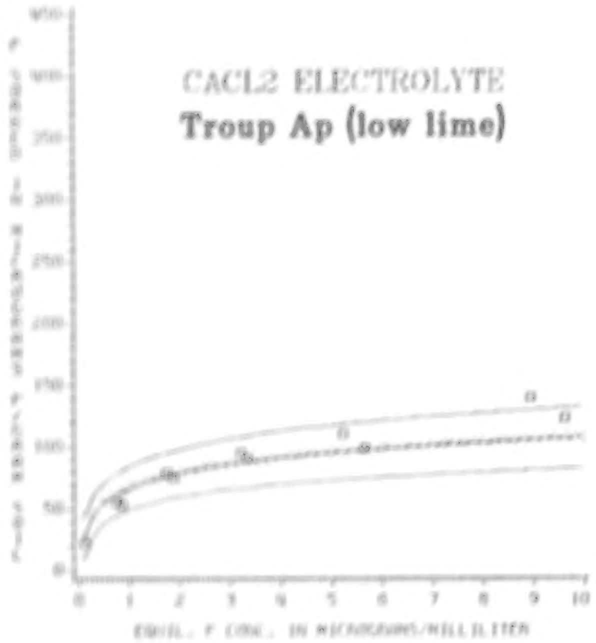
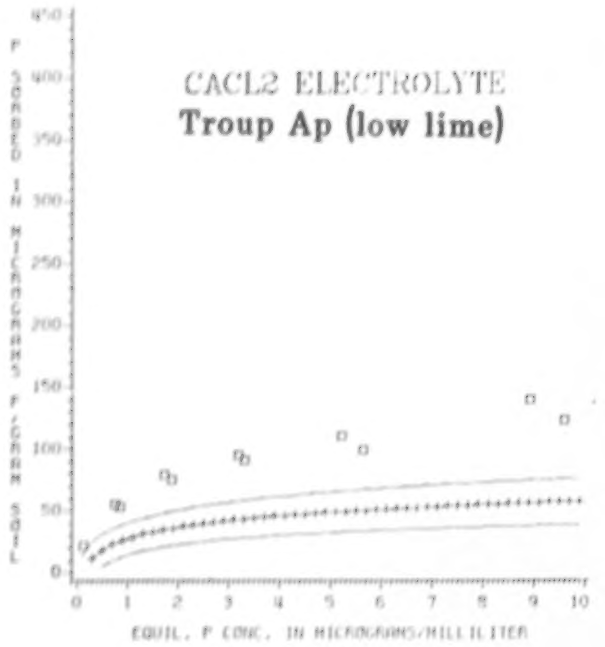
X = B1 CA & CLA1, + = B1 AL2 & CLA1
SOLID LINE=95% CONF. INT. ABOUT CALCULATED ISOTHERM



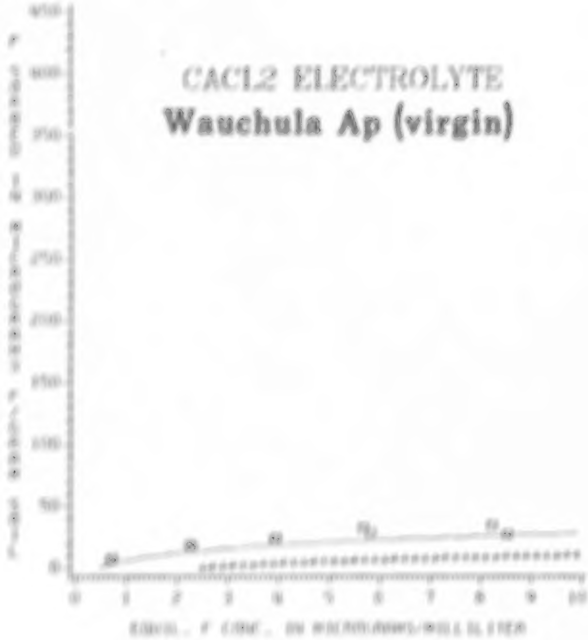


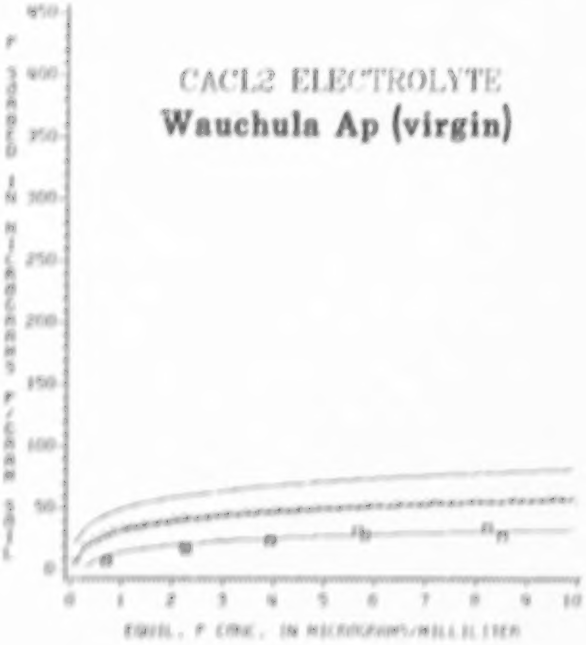
SQUARE=OBSERVED
LINE WITH * OR X = CALCULATED ISOTHERM
X = BY CA & CLAY, * = BY AL2 & CLAY
SOLID LINE=95% CONF. INT. ABOUT CALCULATED ISOTHERM



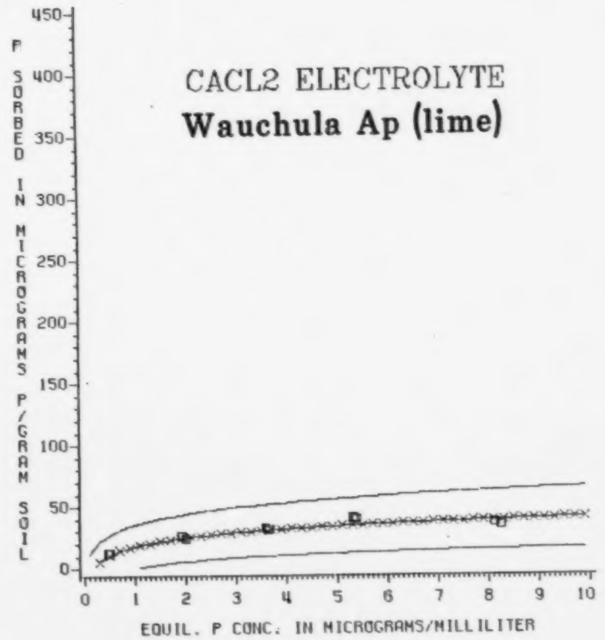


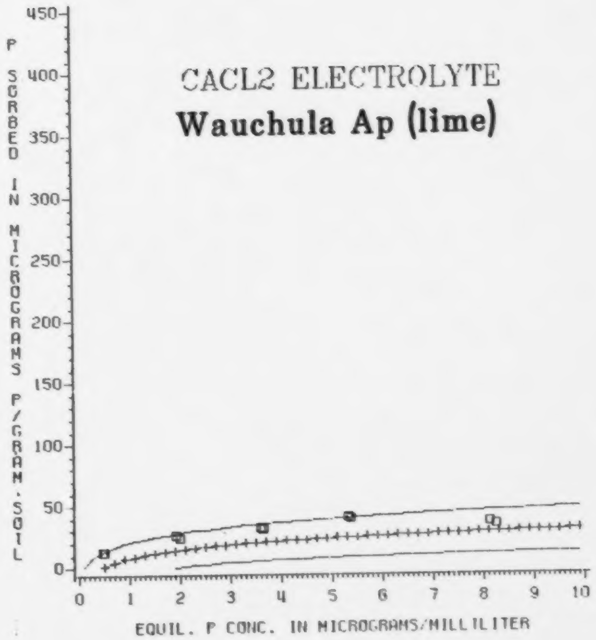
SQUARE=OBSERVED
LINE WITH * OR X = CALCULATED ISOTHERM
X = E1 CA & CLAY, * = B1 AL2 & CLAY
SOLID LINE=95% CONF. INT. ABOUT CALCULATED ISOTHERM





SQUARE =OBSERVED
LINE WITH * OR + = CALCULATED ISOTHERM
* = B(CA & CL2), + = B(AL2 & CL2)
SOLID LINE=95% CONF. INT. ABOUT CALCULATED ISOTHERM





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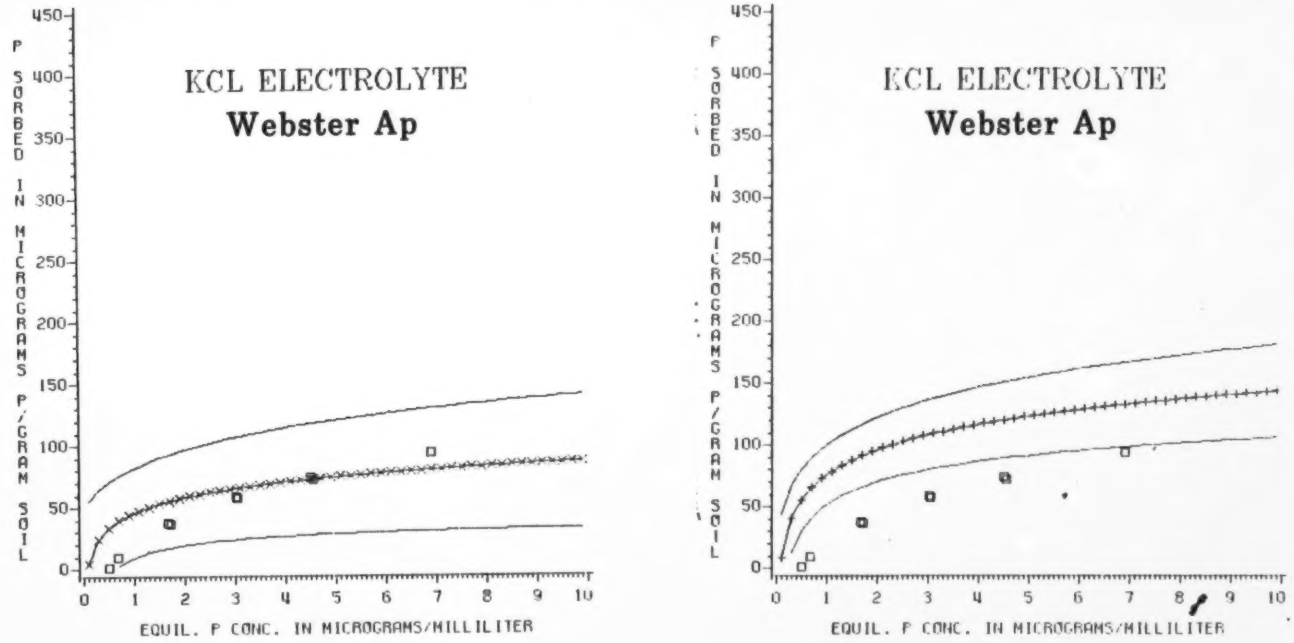

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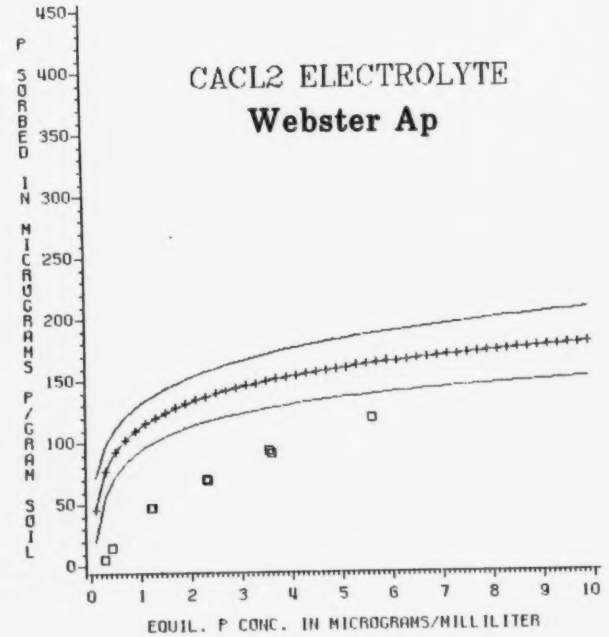

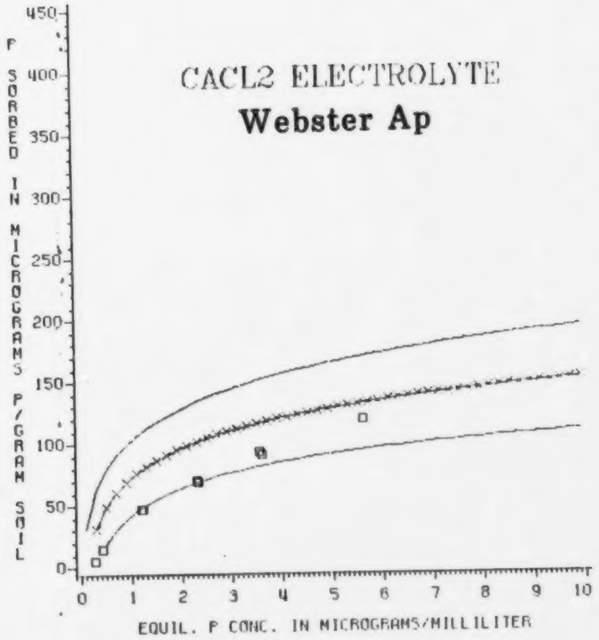

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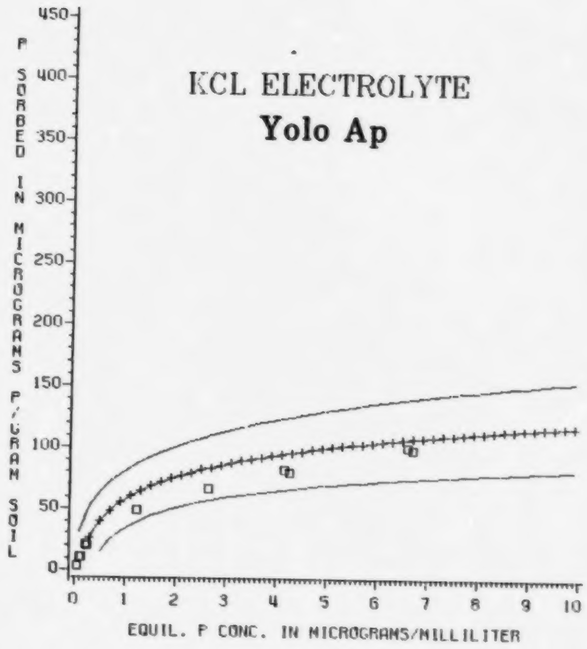

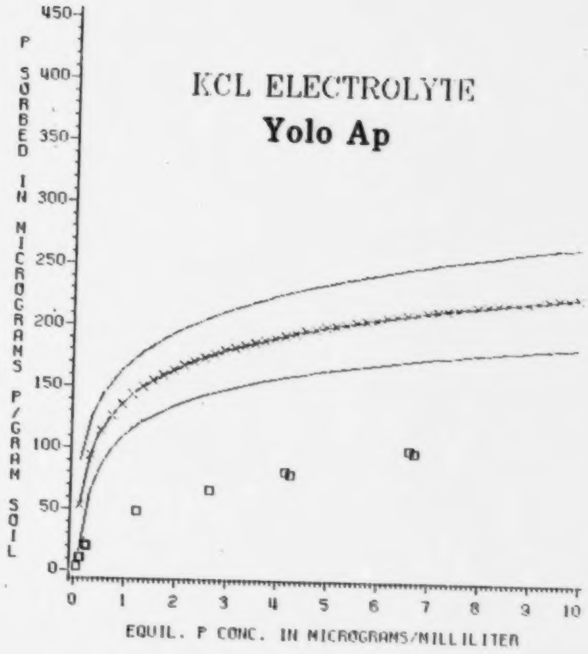

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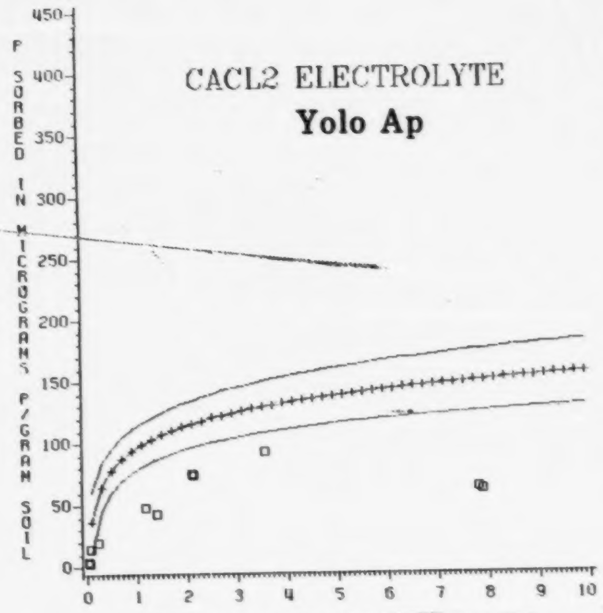

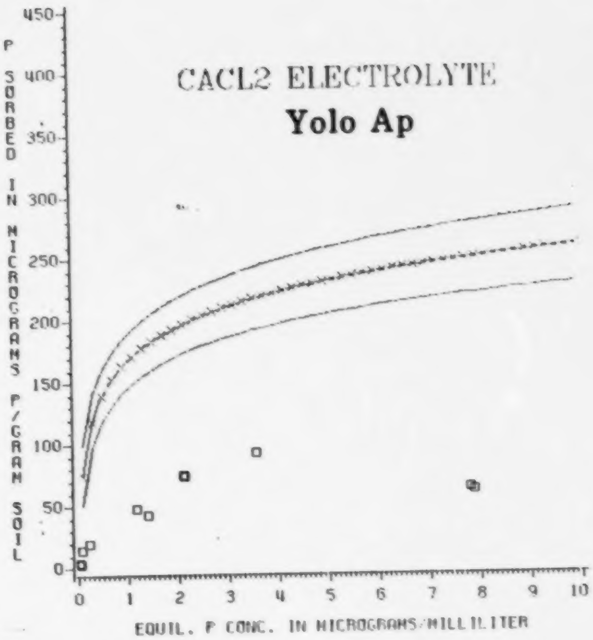

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